

CHAPTER 2

TECHNOLOGY DESCRIPTION AND UNDERLYING PHYSICAL PROCESSES

2-1. Introduction. This chapter presents an overview and general description of dual-phase extraction and two-phase extraction, the latter of which includes a related technology, bioslurping. The three main strategies for applying MPE that will be discussed are: a) vacuum-enhanced recovery of NAPL, b) vacuum dewatering to enable SVE and/or BV to remove and/or treat organic contaminants via the gas phase, and c) vacuum-enhanced recovery of groundwater. This chapter also presents a review of the fundamentals of multiphase flow in porous media, and an assessment of the effectiveness and limitations of the technologies.

2-2. Description of MPE Technologies and Application Strategies.

a. Technology Definitions and Descriptions. MPE comprises a generic category of in-situ remediation technologies that simultaneously extract more than one fluid phase from wells or trenches. These phases generally include air (i.e., gaseous phase including organic vapor) and water (i.e., aqueous phase including dissolved constituents), and may include NAPL. The terminology presented by EPA (1997a), which distinguishes between dual-phase and two-phase extraction technologies, is as follows:

(1) In dual-phase extraction (DPE), soil gas and liquids are conveyed from the extraction well to the surface in separate conduits by separate pumps or blowers. A common "pipe within a pipe" configuration is depicted in Figure 2-1. It shows that a submersible pump suspended within the well casing extracts liquid, which may be NAPL and/or groundwater, and delivers it through a water extraction pipe to an aboveground treatment and disposal system. Soil gas is simultaneously extracted by applying a vacuum at the well head. The extracted gas is, in turn, conveyed to a gas-liquid separator prior to gas phase treatment. DPE is in essence a rather straightforward enhancement of SVE, with groundwater recovery being carried out within the SVE well. Other DPE configurations are also common, such as use of suction (e.g., exerted by a double-diaphragm pump at the ground surface) to remove liquids from the well, rather than a submersible pump (Blake and Gates 1986). A line-shaft turbine pump could also be employed to remove liquids from the well, provided the water table is shallow enough.

(2) In two-phase extraction (TPE), soil gas and liquid are conveyed from the extraction well to the surface within the same conduit, which has been referred to with various names including drop tube, slurp tube, stinger, lance, or suction pipe. A single vacuum source (vacuum pump or blower) is used to extract both liquid and gaseous phases. A common configuration is depicted in Figure 2-2. The suction pipe suspended within the well casing can extract a combination of NAPL and/or groundwater, and soil gas. These phases are conveyed to an aboveground gas-liquid separator. If extraction of NAPL is anticipated, an oil-water separator may be installed downstream of the gas-liquid separator.

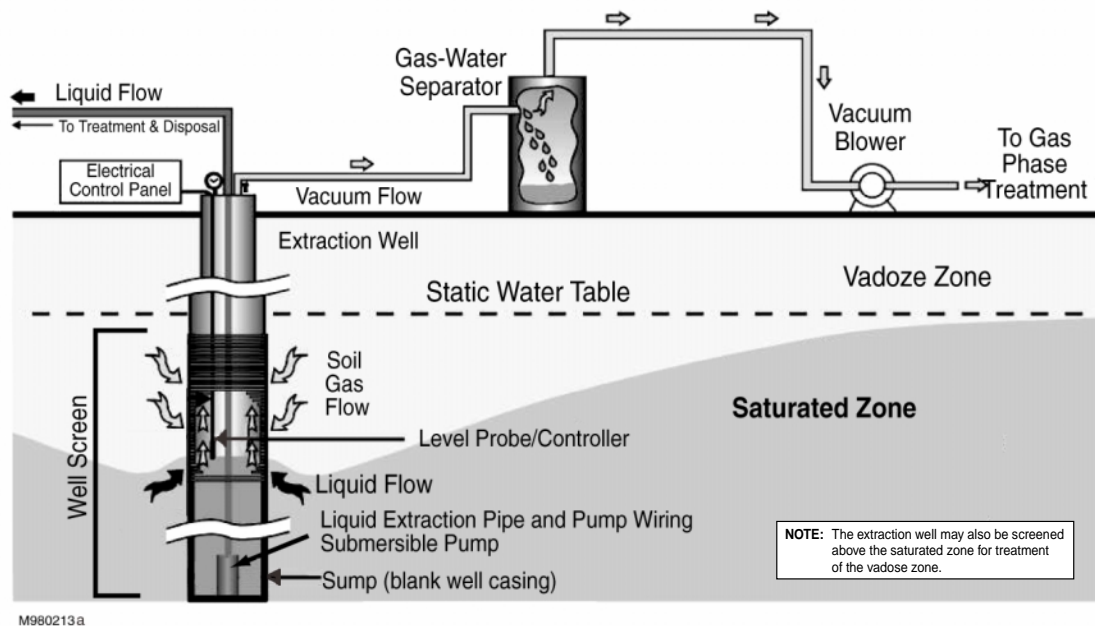


Figure 2-1. Schematic of DPE System (Low Vacuum, or High Vacuum).
(After EPA 1997)

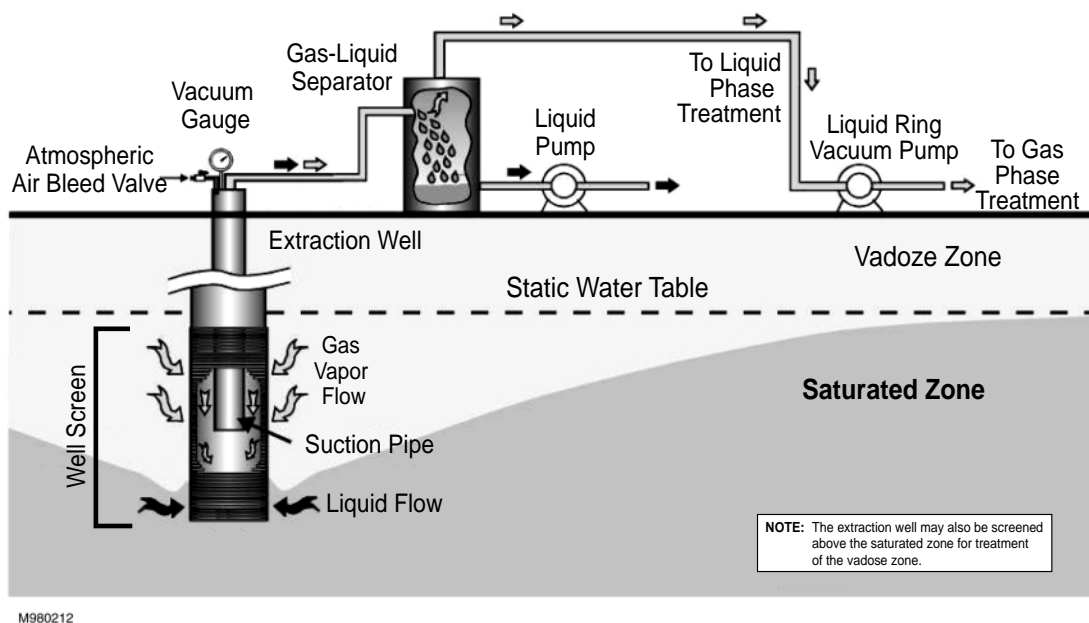


Figure 2-2. Schematic of a TPE System. After EPA 1997)

(3) Bioslurping is a form of TPE that aims to enhance the recovery of LNAPL, while also stimulating BV within the unsaturated zone (AFCEE 1994a; Kittel et al. 1994; AFCEE 1997). A bioslurper uses a suction tube positioned at the LNAPL-water interface to induce a pressure gradient causing water, LNAPL and gas to flow into the well (Figure 2-3). As with TPE, water and/or LNAPL that is drawn into the well is lifted and conveyed to a gas-liquid separator. The liquid phase is subsequently conveyed to an oil-water separator. Bioslurping systems are designed and operated in a manner that maximizes LNAPL recovery while minimizing groundwater and gas-phase recovery. Therefore, the BV aspect of bioslurping is less important than the primary objective of enhancing free-product recovery.

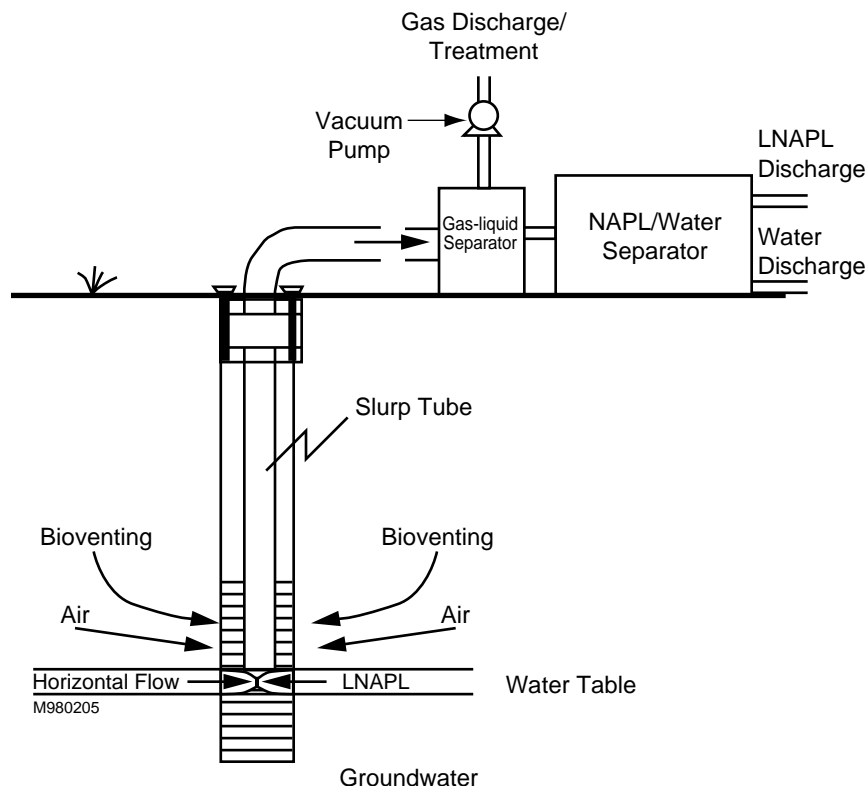


Figure 2-3. Bioslurper System. (After AFCEE 1994b)

b. MPE Application Strategies. One generally chooses MPE to enhance the extraction of one or more of the following phases:

- NAPL, to accomplish free product recovery.
- Soil gas, to accomplish mass reduction through SVE or BV in soils having low air permeabilities.
- Groundwater, to improve pump-and-treat yields. (This objective is the least common of the three.)

(1) These application strategies may be pursued separately or in combination. For example, a reason for implementing MPE may be to accomplish

contaminant mass removal from saturated zones via both gas- and liquid-phase extraction; another may be to improve mass removal from the vadose zone primarily via gas-phase extraction.

(2) One should decide at the outset which strategy is being pursued, because efforts to achieve more than one simultaneously can sometimes be at cross-purposes. For example, an extraction system designed to optimize the recovery of NAPL will probably not be optimal from the standpoint of recovering soil water to enhance SVE. Conversely, a system designed to enhance SVE will probably not do an optimal job of extracting NAPL. In the case of bioslurping, however, both NAPL extraction and BV can be conducted quite compatibly. The ramifications of these differing goals will become clear in subsequent sections.

2-3. General Concepts.

a. Introduction to NAPL and its Transport through Porous Media.

(1) Commercial, industrial and military facilities often use fuels, solvents or other organic chemicals. In the course of transporting, using or storing organic liquids, many of these facilities have experienced releases to soil and groundwater. For example, of the 2 million underground storage tanks (USTs) in the U.S., approximately 295,000, or more than 15 percent were reported to be leaking (USEPA 1993a). Following a spill or release from such storage tanks, piping, and related equipment, many organic contaminants such as those in fuels and solvents enter the soil as oily liquids (Figure 2-4). Because these compounds are not highly soluble in water, they are often present as an immiscible (non-aqueous) phase. This separate liquid phase persists when in contact with water and can serve as a long-term source of groundwater contamination. We term such a fluid a NAPL. We further distinguish between NAPL that has a density less than water (such as gasoline or fuel oil) and one that is more dense than water (e.g., a chlorinated solvent such as trichloroethene) by terming the former a light NAPL (LNAPL), and the latter a dense NAPL (DNAPL).

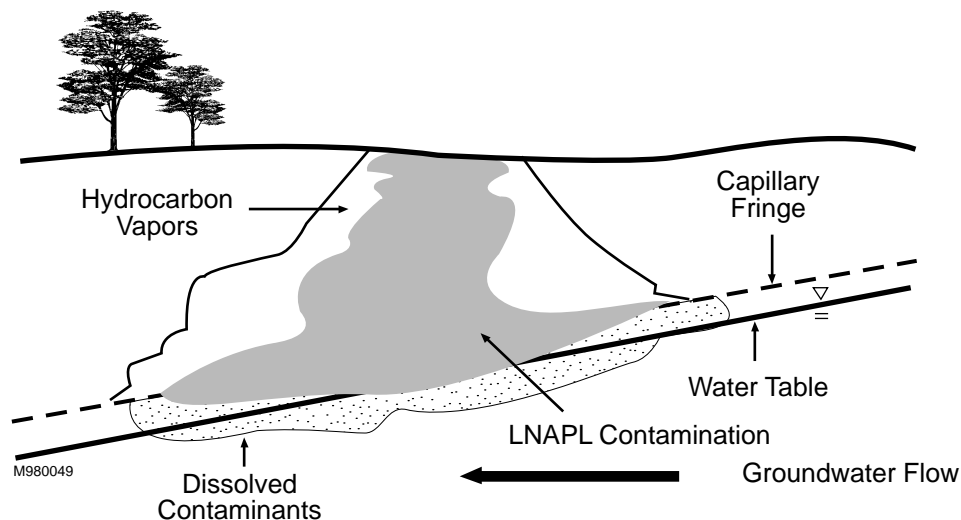


Figure 2-4. Simplified Conceptual Model for LNAPL Release and Migration. (After Newell et al. 1995)

(2) LNAPL poured into a container of water will, at equilibrium, float on the water surface; DNAPL, by contrast, will sink to the bottom of the container. The behavior of NAPL in porous media is more complex, however. When NAPL is released in unsaturated soil, it infiltrates downward under the influence of gravity, and depending on the volume of NAPL that is released, it will proceed toward the water table. As it infiltrates, a fraction of the mass will be left behind, retained by capillary forces of adhesion and cohesion, in the form of globules and ganglia occupying the soil pores and adsorbed to soil particles. This residual NAPL saturation thereby depletes the contiguous NAPL mass until it can infiltrate no further. An encounter with a low permeability layer can also impede its progress. If LNAPL arrives at the capillary fringe above the water table, its buoyancy will limit its further downward migration, but as it accumulates it will hydrostatically depress the capillary fringe and the water table to a certain extent and may move laterally as well (After Mercer and Cohen 1990). Due to its greater density, DNAPL that arrives at the capillary fringe can exert pressures in excess of pore pressures. DNAPL can penetrate the water table and proceed to displace water and infiltrate to greater depths. DNAPL too will deplete itself as it infiltrates, and its movement will be impeded by low permeability layers or bedrock fractures with small apertures. Even so, DNAPL has penetrated to significant depths beneath the water table and within fractured bedrock at many sites (Pankow and Cherry 1996).

b. Contaminant Phase Distribution. Residual or mobile NAPL residing in the subsurface, whether LNAPL or DNAPL, serves as a long-term source for contamination of groundwater (Figure 2-5). When NAPL is present at a site, it typically represents the largest fraction of the contaminant mass. For example, most of the contaminant mass in cases of LNAPL releases is in the smear zone (refer to paragraph 2-4b(2)). In addition to being present as (1) NAPL, the contaminants partition into three other principal phases, as follows. (2) Soluble components of the NAPL dissolve into infiltrating precipitation and groundwater that come into contact with it, creating an *aqueous-phase* groundwater plume (or plumes) emanating from the source zone(s). (3) Volatile components of the NAPL and of the aqueous-phase (soil pore water and groundwater) partition into the *gas phase*, which is itself capable of migrating through the unsaturated zone. (4) Contaminants in the NAPL, aqueous, or gas phases partition into the *solid phase* with which they are in contact. Solid phase sorbants include the inorganic and organic materials in the soil or aquifer, particularly clay minerals that have the greatest specific surface (surface area per unit of mass) to which contaminants can adsorb, and humic materials for which organic compounds have a high affinity. Thus the greater the clay and/or organic content of the soil and aquifer materials, the larger will be the fraction of the contaminant mass that can be adsorbed to them. The partitioning of volatile organic compounds (VOCs) among these four phases, and definitions of the pertinent partitioning coefficients (i.e., solubility, Henry's Law constant, vapor pressure and soil/water distribution coefficient) used to quantify the tendency of specific contaminants to distribute themselves among these phases are described in more detail in EM 1110-1-4001, Soil Vapor Extraction and Bioventing, Chapter 2, Contaminant Properties.

c. NAPL Recovery. If a subsurface zone containing NAPL (i.e., a source zone) is present at a site, the most efficient way to remove contaminant mass is direct extraction of the NAPL itself, if it is amenable to recovery. Furthermore, free-product recovery to remove the bulk of the floating product is generally considered a prerequisite to the application of in-situ technologies, such as BV, that require a well-aerated soil for spatially distributed microbial growth and hydrocarbon degradation (Baker 1995). The successful removal of NAPL depends greatly on the method of free-product recovery that is selected.

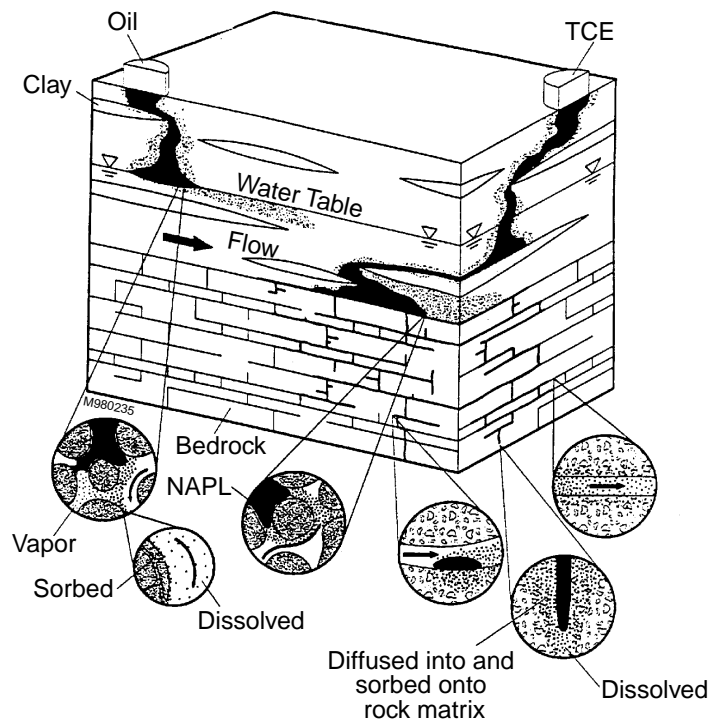


Figure 2-5. Distribution of Phases in the Subsurface. (USEPA 1995)

(1) Conventional LNAPL Recovery. Where floating product forms a continuous, free-phase layer on the water table, and especially in coarse-textured soils (e.g., sand and gravel), conventional modes of free-product recovery using submersible and skimmer pumps in wells/trenches are generally effective (API 1996; USEPA 1996). Submersible pumps generally extract NAPL and water, whereas skimmer pumps can extract LNAPL only. Submersible single- or double-pump systems (Figure 2-6a and b) extract groundwater and product and thus create a cone of depression in the water table. The resulting drawdown produces a hydraulic gradient, causing floating product to flow into the well. Because water that has been in contact with NAPL is also recovered, it must be treated prior to discharge. Skimmer systems (Figure 2-7) recover floating product only and do not usually induce a significant cone of depression. Floating filter scavenger systems, for example, can remove product down to thin layers as they track fluctuations in the water table. Although recovery rates are generally smaller, skimmer systems have the advantage that treatment of water is not required. Such systems tend to be most suitable for highly permeable formations, or where recovery rates would not be sufficient to justify operation of more costly combined water and product recovery systems. Absorbent bailers and belt skimmers also fall within this category, but are suitable only when very low rates of product recovery are acceptable. Table 2-1 presents a range of free-product recovery approaches and relative advantages and disadvantages of each. Note that pneumatic transfer of flammable liquids by air pressure (in direct contact with the liquid) is prohibited by EM 385-1-1. If pneumatically operated pumps are used, it must be ensured that the air supply is 100% isolated from free product. Most pneumatic remediation pumps sold today and/or operating today keep the motive air

separate from the pumped liquid; therefore, they do not violate this prohibition.

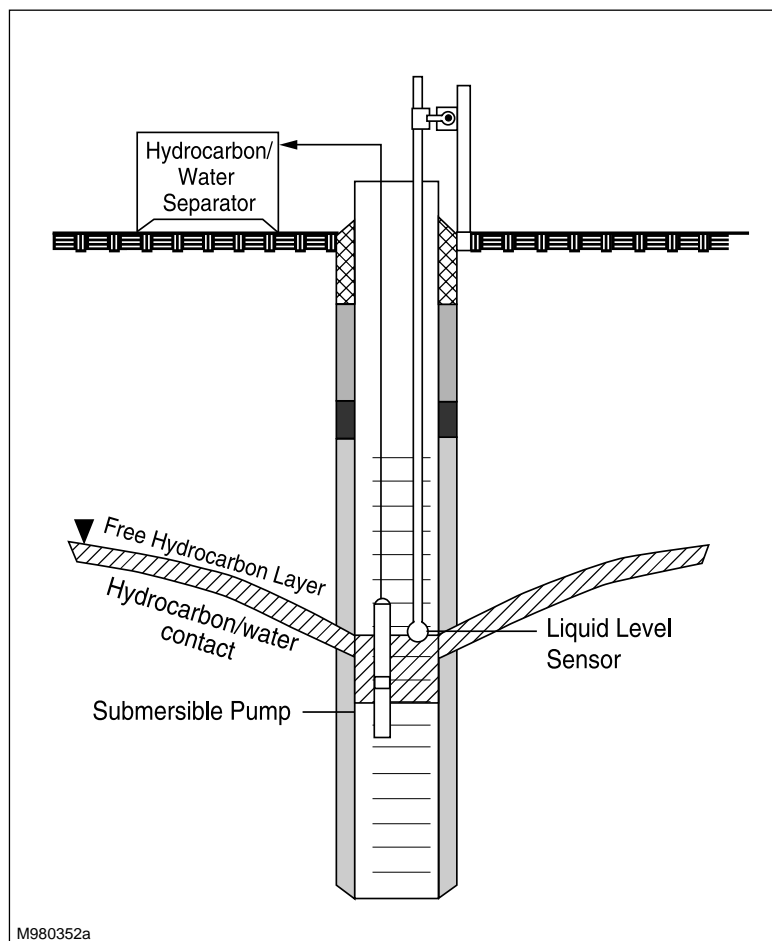


Figure 2-6a. Conventional LNAPL Recovery Using Single-Pump System. (After API 1996. Reprinted by permission of American Petroleum Institute. Copyright 1996. All rights reserved.)

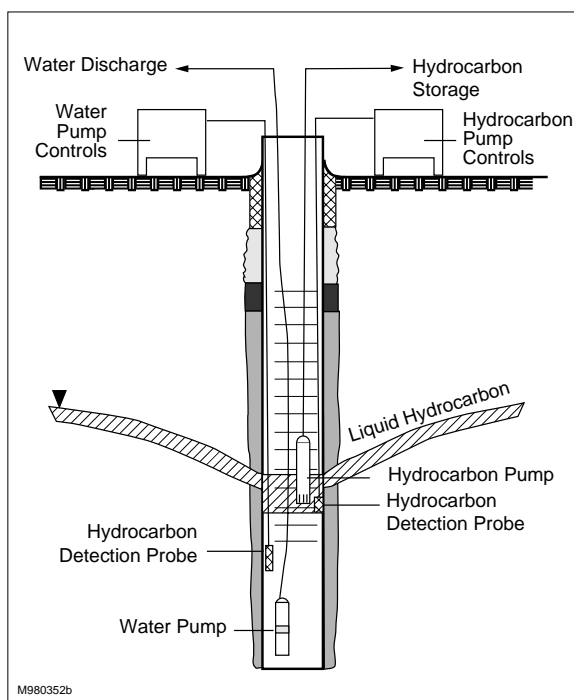


Figure 2-6b. Conventional LNAPL Recovery Using Two-Pump System.
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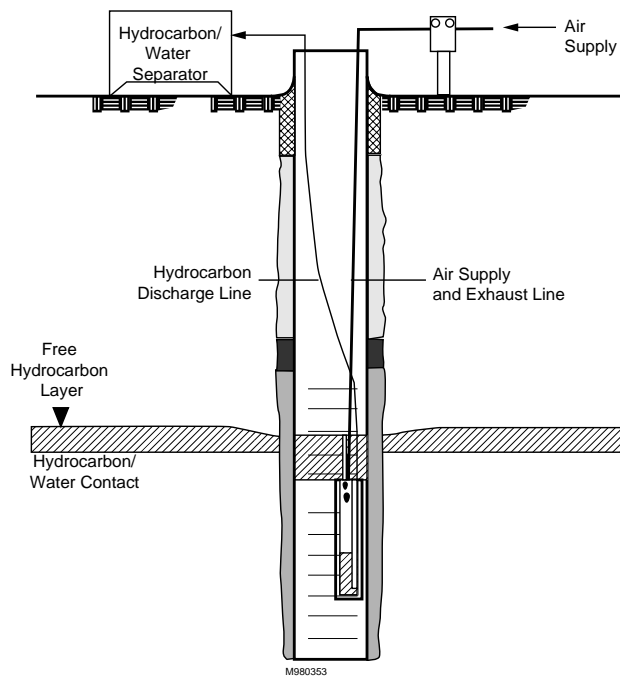


Figure 2-7. Pneumatic Skimming Pump. (After API 1996. Reprinted by permission of American Petroleum Institute. Copyright 1996. All rights reserved.)

TABLE 2-1
Free Product Recovery and Control Systems and Equipment
(After USEPA 1996a)

	Recommended Minimum Well Diameter	Recommended Minimum Value for K (cm/sec)	Relative Capital Costs	Relative Operating Costs	Relative Maintenance Costs	Potential for Product Removal	Advantages	Disadvantages
SKIMMING SYSTEMS								
• Floating								
- Large Saucer Type	36"	$>1 \times 10^{-4}$	L	L	M	M	No water pumped, skims very thin layers, moves up and down with GW	Limited radius of influence, clogging of screen, generally limited to shallow (<25 ft) applications
- Small Float Type	4"	$>1 \times 10^{-4}$	L	L	M	M		
• Floating inlet								
- Bailer/Passive	2"	$>1 \times 10^{-4}$	L	L	L	L	No water pumped, skims very thin layers, low cost	Limited radius of influence, manually adjusted, clogging, low removal rate (different for bailers and pneumatic pumps)
- Pneumatic Pump	4"	$>1 \times 10^{-4}$	L	L	L	L		
• Absorbent								
- Absorbent Bailer	2"	$>1 \times 10^{-4}$	L	L	L	L		
- Belt Skimmer	2"	$>1 \times 10^{-4}$	L	L	L	L		
SINGLE PUMP SYSTEMS								
• Diaphragm Pump	2"	$>1 \times 10^{-4}$	L	L	L	L	Low cost, low maintenance surface-mounted pumps, easy to maintain, low flows	Pumps water and product, requires o/w separator, shallow (<20 ft)
• Centrifugal Pump	2"	$>5 \times 10^{-3}$	L	L	L	L	Low cost and maintenance	Level sensor and o/w separator required (<25 ft)
• Submersible Pump	4"	$>1 \times 10^{-2}$	M	M	L	L	No depth limitation, easy installation, removes water and product	Flow >5 gpm, o/w separator water treatment, emulsification
• Pneumatic								
- Top Filling	4"	$>1 \times 10^{-3}$	M	M	M	M	Can operate over wide range of flow rates, can pump from deep, low K aquifers	Requires air compressor system and water treatment, emulsification
- Product only	4"	$>1 \times 10^{-4}$	M	M	M	M		

TABLE 2-1
Free Product Recovery and Control Systems and Equipment
(After USEPA 1996a) (Continued)

	Recommended Minimum Well Diameter	Recommended Minimum Value for K (cm/sec)	Relative Capital Costs	Relative Operating Costs	Relative Maintenance Costs	Potential for Product Removal	Advantages	Disadvantages
DUAL PUMP SYSTEMS								
• GWP and PP with separate levels and product sensors	8"	$> 1 \times 10^{-2}$	H	H	H	H	Cone of depression induces migration of product to well, high potential product removal rates, pump GW and product potential large radius of influence	High initial cost, high maintenance; recovery wells often become clogged and inefficient, works best in clean sands and gravels, cycling the GWP on and off with level sensor not recommended approach
• GWP running steady with PP and product sensor	6"	$> 1 \times 10^{-2}$	H	H	M	H		
• GWP running steady with floating product skimming pump	6"	$> 1 \times 10^{-3}$	H	H	M	H		
DIRECT REMOVAL								
• Open Excavations or trenches	L	...	M	Good initial remedial action using vacuum truck absorbent pads, etc.	Not practical for removing product away from excavation area
• Routine skimming or bailing of wells	2"	$> 1 \times 10^{-4}$...	L	...	L	Inexpensive, works on small localized product layers	Very limited radius of influence and removal rate
VACUUM ENHANCED PUMPING								
• Drop tube suction lift	2"	$> 1 \times 10^{-5}$	M	H	L	VH	Works well with medium permeability soils, large radius of influence, increases water and product flow by 3 to 10 times; can significantly reduce site remediation time	Requires high vacuum pump or blower, usually requires thermal air treatment system and water treatment
• In-well pump augmented by vacuum on well	4"	$> 1 \times 10^{-5}$	H	H	L	VH		

a GW = Groundwater
GWP = Groundwater Pump
PP = Product Pump
K = Hydraulic Conductivity
GPM = Gallons Per Minute

L = Low
M = Medium
H = High
VH = Very High

Approximate cost ranges based on a unit single well system including water handling and treatment:

Capital Costs:	L = \$3,000-10,000	Operating Costs:	L = \$500-1,000/mo	Maintenance Costs:	L = <10% of capital cost/yr
	M = \$10,000-25,000		M = \$1,000-3,000/mo		M = 10 to 25% of capital cost/yr
	H = >\$25,000		H = >\$3,000/mo		H = >25% of capital cost/yr

(2) Vacuum-Enhanced LNAPL Recovery. Vacuum-enhanced free-product recovery (Blake and Gates 1986; Hayes et al. 1989; API 1996) is employed, usually in medium-textured soils, to increase recovery rates of LNAPL relative to those that can be obtained using conventional means. The application of a vacuum to a recovery well increases the extraction flow rate without inducing a physical cone of depression (Blake and Gates 1986). In cases where physical drawdown is used in combination with vacuum enhancement, the effective drawdown, by superposition, is the sum of the induced vacuum (expressed in water equivalent height) and the physical drawdown (Figure 2-8). The gradient of hydraulic head that is the driving force for flow of liquid to the well is thus increased. Consequently, the volume of water extracted typically increases to an even greater extent than does the volume of LNAPL. Vacuum-enhanced recovery may also mobilize some of the LNAPL that would not otherwise be able to drain into a well because it is retained by capillary forces (Baker and Bierschenk 1995). Offsetting the increase in LNAPL removal is the necessity to treat and/or discharge a larger volume of extracted groundwater and an extracted gas stream.

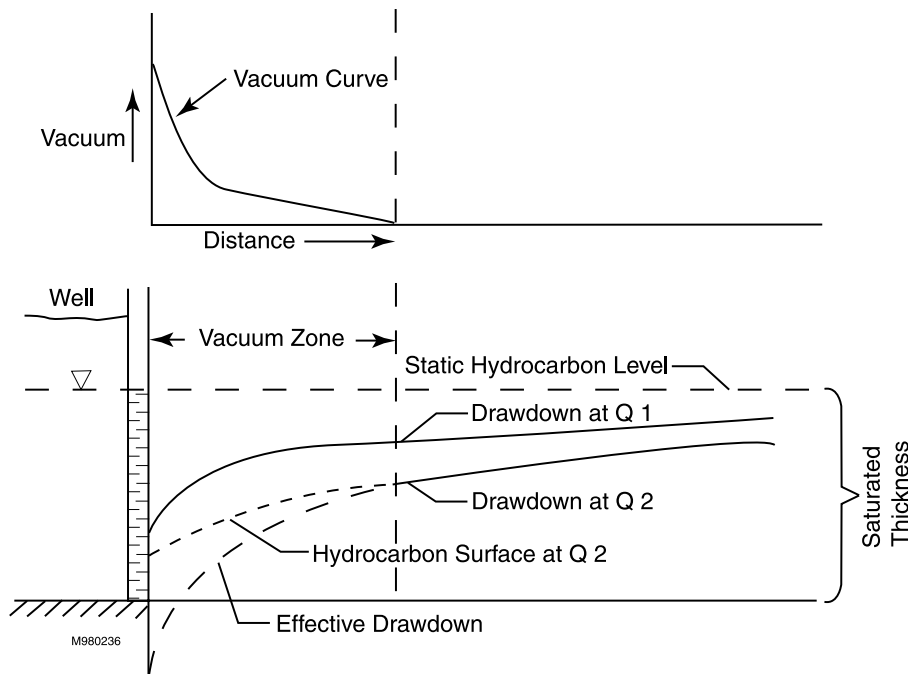


Figure 2-8. Schematic of Vacuum Effect on Perched Hydrocarbons. Q1 is extraction rate without application of vacuum; Q2 is extraction rate with application of vacuum. (Blake and Gates 1986. Reprinted by permission of National Ground Water Association. Copyright 1986. All Rights reserved.)

d. Dewatering to Enable SVE/BV.

(1) In low to moderately permeable formations that are in relatively close proximity to the capillary fringe, SVE and BV tend to have limited effectiveness, because while air can flow through air-filled passages, it cannot flow through pores in such formations that tend to be saturated with water. The process of applying a vacuum to the soil to accomplish SVE also causes the water table to rise locally, further limiting the zone through which air can flow. By removing both water and gas from the subsurface, these limitations, to some extent, can be overcome. Vacuum dewatering (Powers 1992) has had decades of use in the construction industry, where it is generally used

to remove water from medium- to fine-textured soils that would otherwise flow into excavations made below the water table. Thus it enables excavation to occur and facilitates construction of deep footings and piers. When performed in VOC-contaminated soil, vacuum dewatering permits the flow of air through some of the previously saturated soil, thereby allowing VOCs residing there to partition into the air stream (Figures 2-1 and 2-2). In addition, soluble VOCs present in the extracted groundwater are also removed (USEPA 1997a). When carried out in soils contaminated with semi-volatile organic compounds (SVOCs) that biodegrade under aerobic conditions, vacuum dewatering enhances the aeration of previously saturated soil, thus stimulating in-situ aerobic biodegradation. It can also result in an increase in the dissolved oxygen (DO) content of soil pore water, helping to further enhance aerobic biodegradation in soil that is not able to be desaturated. The potential effectiveness of this process relative to other available alternatives that do not necessarily involve extraction and treatment of groundwater, such as in-situ air sparging (IAS) and in-situ groundwater bioremediation, needs to be considered on a site-specific basis.

(2) It is important to underscore that compared to most other regions above the water table, the zone where air permeability is quite low (the capillary fringe) will transmit very little airflow during SVE or BV operation. Since in the case of LNAPL releases, this zone also tends to contain much residual LNAPL contamination (i.e., within the unsaturated portion of the smear zone), the problem of addressing the residual LNAPL is compounded unless the smear zone can be dewatered and exposed to airflow (Mickelson 1998). MPE offers a means to overcome this problem (Peargin et al. 1997).

e. Vacuum-Enhanced Pump-and-Treat. At times, particularly in moderate- to low-permeability formations, groundwater pump-and-treat extraction rates can fail to meet pre-specified hydraulic targets. A number of factors can contribute to this problem, including inadequate characterization of the hydrogeological system, failure in selecting appropriate well-screen intervals and pumps, mechanical/operational problems, well fouling, and changes in groundwater geochemistry resulting from the extraction process. If mechanical problems and limitations have been addressed, extraction rates can usually be enhanced simply by increasing the drawdown. If the physical drawdown cannot be further increased, however, e.g., because doing so would exceed the available saturated thickness, another option is to apply a vacuum gradient to the extraction well. The addition of the applied vacuum gradient to the gravitational gradient associated with physical drawdown produces an effective drawdown that can exceed the available saturated thickness, as illustrated in Figure 2-8 (Blake and Gates 1986). Consequently, the groundwater yield can be enhanced. This technique is being applied by the USACE, Philadelphia District, at the Lipari Landfill Superfund Site. DPE, rather than TPE, is the approach of choice to accomplish vacuum-enhanced pump-and-treat, because it offers a more cost-effective means of pumping groundwater.

2-4. Fundamentals of Multiphase Flow in Porous Media. An understanding of the basic concepts and physical processes involved in multiphase fluid flow is a prerequisite to making appropriate use of MPE. Much of the theory that will be presented in this section is derived from soil physics (Parker 1989; Baker 1998) and petroleum engineering (e.g., Corey 1986).

a. Constitutive Relations for Multiphase Flow and Hydrostatics.

(1) Saturation. The volume fraction of pores occupied by a given fluid is its saturation, such that water saturation, S_w , is defined as

$$S_w = \frac{V_w}{V_{pores}} \quad [2-1]$$

where V_w = volume of water, and

V_{pores} = volume of pores.

(Note that $V_{pores}/V_t = n$, where V_t = total volume of soil under consideration, and n = porosity.) Following Equation 2-1, organic liquid and air saturations, S_o and S_a , are the volume fractions of the pores occupied by NAPL and by air (or other gas), respectively. It therefore holds that for any given representative elementary volume in porous media,

$$S_w + S_o + S_a = 1 \quad [2-2]$$

Note that field and laboratory measurements are not usually expressed in terms of saturation, so appropriate conversions need to be performed. Moisture content, for example, is typically expressed as the amount, by weight or volume, of water in a soil. When given on a mass basis, moisture content, w , is the mass of water in a soil sample, M_w , divided by its oven-dry mass, M_{soil} ; or $w = M_w/M_{soil}$. When expressed on a volume basis, moisture content, θ , is the volume of water in a sample, V_w , divided by the total bulk volume of the sample, V_t ; or $\theta = V_w/V_t$. Thus from Equation 2-1 and the definition of porosity, $S_w = \theta/n$. To obtain volumetric moisture content from gravimetric moisture content, use the relation $\theta = w\rho_b/\rho_w$, where ρ_b is the bulk density (i.e., the dry weight of soil per bulk unit volume) and ρ_w is the density of the reference fluid, water.

(2) Capillary Pressure. When two or more immiscible fluids coexist in a porous medium, the pressure difference that is manifest across the fluid-fluid interface is termed the capillary pressure, P_c , defined as:

$$P_c = P_n - P_w \quad [2-3]$$

where: P_n = pressure in the nonwetting phase, and

P_w = pressure in the wetting phase.

The wetting fluid is that which has a greater affinity for the solid phase and occupies the smaller pores, while the nonwetting fluid is consigned to the larger ones and is at the higher pressure, such that the interface between them is concave toward the nonwetting phase (Brooks and Corey 1964; Parker 1989). Thus by definition, $P_n > P_w$, so P_c ordinarily must be positive. Dividing Equation 2-3 through by ρ_w and g , gravitational acceleration, we obtain an equivalent definition for capillary pressure head (or simply "capillary head"):

$$h_c = h_n - h_w \quad [2-4]$$

where: h_n = non-wetting capillary head, and

h_w = wetting capillary head.

The direction of motion of individual fluids is determined by the boundary conditions (in terms of pressure, including capillary pressure, and elevation) imposed on the individual fluids.

(3) Relationship between Saturation and Capillary Head. If the orientation of the fluid-fluid interface is not affected by gravity or adsorptive forces, then the radius of curvature of the interface, r , is related to the capillary head by Laplace's equation of capillarity:

$$r = \frac{2\sigma_c \cos \alpha}{\rho_w g h_c} \quad [2-5]$$

where: σ_c = the interfacial tension between the two fluids, and

α = the wetting angle of the liquid on the solid phase.

The air-oil, oil-water, or air-water interfacial tensions are designated σ_{ao} , σ_{ow} and σ_{aw} , respectively; the air-water interfacial tension is more commonly termed the surface tension. With a gradual reduction in the capillary head at a location in porous media, a nonwetting phase will progressively be displaced by a wetting phase, and conversely with a gradual increase in the capillary head, the wetting phase will be displaced by the nonwetting phase. Either way, the relative fluid saturations must change. For an air-NAPL-water fluid system in water-wet soil, S_w depends on the h_c value between water and NAPL phases; and the total liquid saturation, $S_t = S_w + S_o$, depends on the h_c value between the NAPL and gas phases (Lenhard and Parker 1990; Parker et al. 1996). The relationship between capillary head and saturation, $h_c(S)$, for either fluid pair is a function of the pore size distribution of the soil. Measuring the $h_c(S)$ relationship is one of the best ways to understand the pore size distribution that prevails at specific locations in the soil, and is therefore a good way of predicting how fluids will behave during remediation.

(4) Capillary Model. Rearranging the terms of Laplace's equation of capillarity (Equation 2-5), and assuming a contact angle $\alpha = 0$, the height of capillary rise in a cylindrical glass capillary tube is:

$$h_c = \frac{2\sigma}{\rho_w g r} \quad [2-6]$$

where, for an air-water system, $\sigma = \sigma_{aw}$ (Hillel 1998). This equation states that while the equilibrium height of capillary rise is related to surface tension, it is inversely related to the radius r of the capillary tube. This model can be employed to obtain a simplified representation of the effect of pore size distribution on the water content profile within unsaturated soil.

Consider a vertically oriented bundle of capillary tubes, the lower ends of which sit in a dish of water (representative of the water table). By Equation 2-6, the larger the tube radius, the smaller the height of capillary rise of water within the tubes. Likewise, the smaller the tube radius, the larger the height of capillary rise. A soil consisting entirely of pores of the same radius is like a bundle of identical capillary tubes: the lower portions of all the tubes will be filled with water, but above the height of the menisci, all of the tubes will be empty. A plot of the volumetric water content of the tubes versus height above the free water surface is thus a step function. Again rearranging terms in Equation 2-6, and substituting the equivalency $P_c = \rho_w g h_c$, we obtain:

$$P_c = \frac{2\sigma}{r} \quad [2-7]$$

This form of the capillarity equation indicates that there is a capillary pressure associated with each size pore; the larger the radius, the smaller the capillary pressure and vice versa. A soil having a range of pore sizes can be represented by a bundle of capillary tubes of various radii. The profile of volumetric water content within such a bundle of tubes indicates that as one moves upward from the free water surface, the water content of each horizontal slice across the tubes diminishes in a fashion that is *characteristic* of the pore size distribution. Plots of capillary pressure versus volumetric water content for various soil textural classes (Figure 2-9) are typically obtained from laboratory analyses (paragraphs 2-5e(3) and 3-4g(3)), and are often referred to as *soil moisture characteristic curves*. It is evident from the figure that coarse-grained soils, such as sands, become desaturated (i.e., attain a low water content) at relatively low capillary pressures (e.g., 10 to 20 cm H₂O). By contrast, fine-grained soils, such as silts and clays, retain most of their water content even at much higher capillary pressures (e.g., >500 cm H₂O). It is commonly assumed that these finer-grained soils can be readily dewatered to open their pores to airflow. A large amount of vacuum would be required, however, to overcome such strong capillary forces—more vacuum than will ordinarily propagate into the matrix blocks of a silty clay or finer-textured soil. Thus, these soil properties have a profound influence on MPE effectiveness. The difficulty of dewatering such soil in practice will be discussed in paragraph 2-5e(5)(a).

(5) Air Permeability. The ability of soils to transmit airflow (i.e. their air permeability) varies strongly as a function of both saturation and capillary pressure and differs greatly for various soil types. This is presented qualitatively in Figure 2-10. The pore size distribution of each soil in the figure is represented as a set of cylinders. It should be noted that the range of pore sizes depicted for the sand is actually wider than shown. Pores that are filled with water at a given capillary head are darkened; those that are drained of water at a given capillary head are hollow. The relative air permeability is indicated by the length of the arrows extending from the hollow cylinders. In actuality, the range of air permeabilities would be much greater than can readily be illustrated in this fashion. Note that as water saturation diminishes and air saturation increases accordingly, capillary heads increase. In the process, air permeability is initiated (except in the clay), and increases as one moves toward the upper left corner of the plot. The clay soil will not transmit air, if the clay is uniform, except via desiccation cracks under very dry conditions. The capillary pressure (or capillary head) at which air can first begin to flow through an initially saturated soil is termed the air emergence pressure, and is explained in more detail in paragraph 2-5e(3) and Figure 2-14.

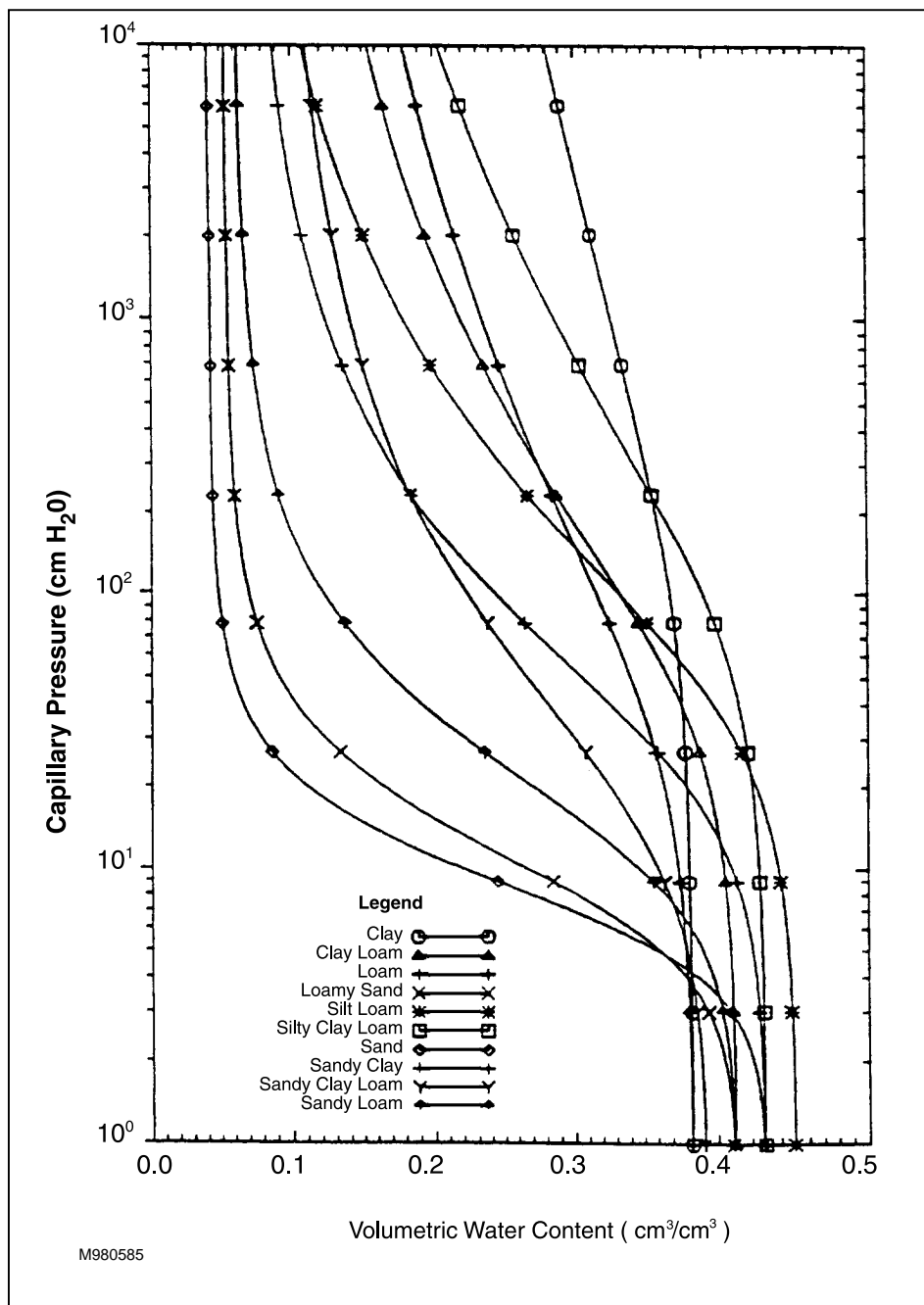


Figure 2-9. Typical curves showing the relationship between capillary pressure and volumetric water content. (USEPA 1991c)

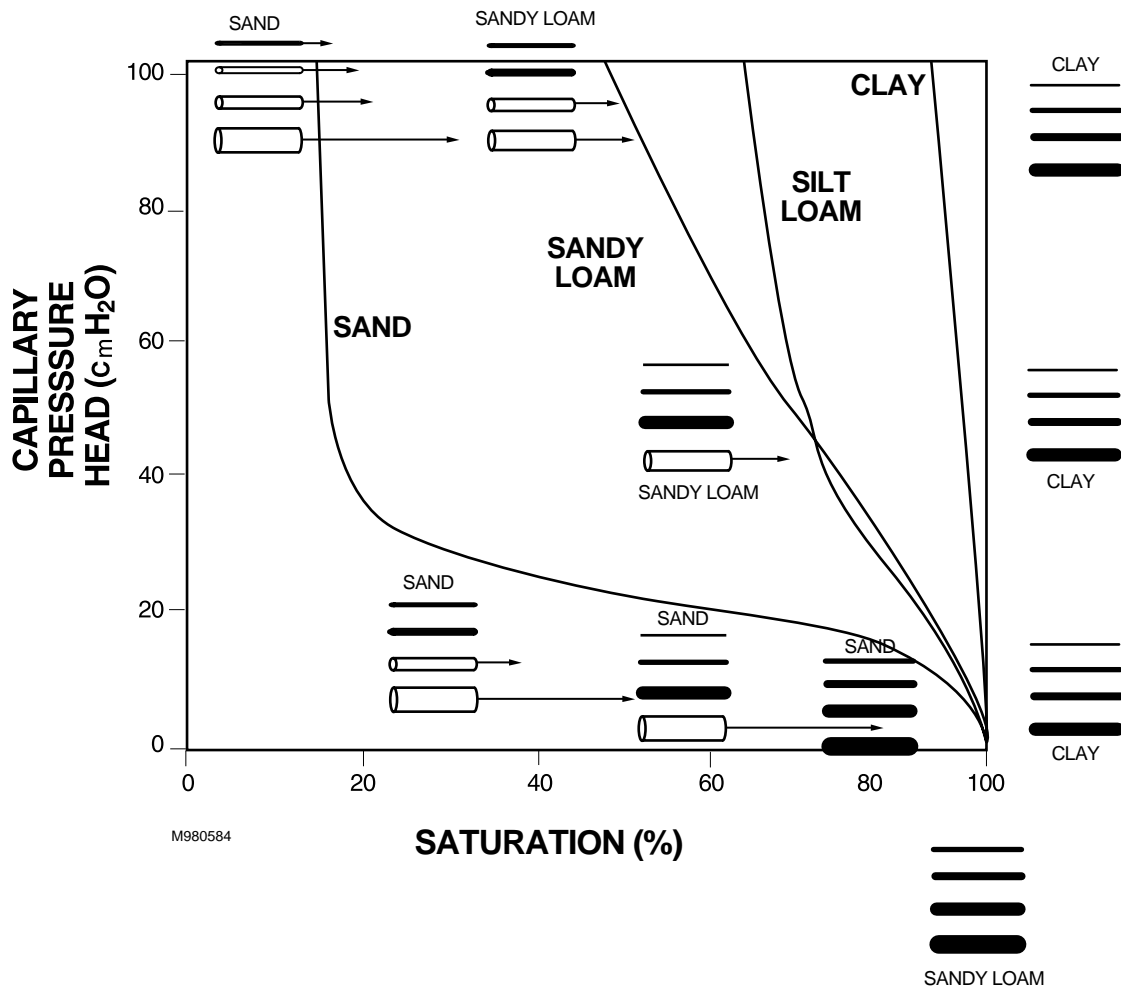


Figure 2-10. Capillary Pressure Head-Saturation Curves and Relative Air Permeability. The pore size distribution of several representative soil types is portrayed as a set of cylinders. Pores that are filled with water at a given capillary head are darkened; those that are drained of water are shown as hollow. The relative air permeability is indicated by the length of the arrows extending from the hollow cylinders. This figure is intended to provide a qualitative representation.

(6) Hysteresis. To complicate matters, the $h_c(S)$ relationship described in paragraphs 2-4a(3) and 2-4a(4) is not unique for a given soil, but exhibits hysteretic effects, i.e., it varies depending on the history of saturation changes. Somewhat higher capillary pressures are typically observed at given saturations during intervals of decreasing wetting phase saturation (drainage) than during increasing wetting phase saturation (imbibition). Although it is convenient to disregard it, hysteresis may need to be taken into consideration particularly when attempting to model the effects of rising and falling water tables on LNAPL entrapment. This is difficult to put into practice, however, due to uncertainties in saturation histories and the possible presence in the subsurface of soils that may exhibit partial hydrophobicity, with some zones being water-wet while others are oil-wet (Kool and Parker 1987; Parker and Lenhard 1987a; Lenhard et al. 1988; Lenhard and Parker 1990).

b. Movement of NAPL: Redistribution and Drainage. Let us now consider the processes by which NAPL moves through the soil.

(1) NAPL Redistribution. As NAPL enters and moves through soil, it depletes itself by leaving behind along its path an amount of NAPL equal to its residual saturation, S_{or} . (S_{or} is the NAPL saturation that remains in a soil that, having contained NAPL, is subjected to drainage until the NAPL-filled pore spaces are no longer contiguous.) If a sufficient volume of LNAPL reaches the water table, it will be affected by buoyancy forces as it accumulates there (Newell et al. 1995), and will then distribute itself within the soil above the water-saturated zone. Its transport will be governed by gradients of hydraulic head, in accordance with Darcy's law (Parker 1989). The dissolved- and gas-phase plumes that arise from NAPL are typically the forms by which the contaminants pose a potential risk to human health and the environment, but a further discussion of their fate and transport is beyond the scope of this chapter.

(2) Smear Zone. As the water table fluctuates, LNAPL will tend to be redistributed upward and downward over the vertical extent of the water table's rise and fall. The processes of NAPL entrapment and retention in the saturated zone (which occur as the water table rises) and retention in the unsaturated zone (as the water table falls) tend to increase the elevation range, termed the *smear zone*, over which $S_o \geq S_{or}$ at many, if not all locations (i.e., some locations may have $S_o \leq S_{or}$). They also tend to reduce the apparent product thickness evident in monitoring wells, particularly as the water table rises, when LNAPL entrapment tends to be greater. It is important to try to identify the smear zone early in the process of developing a conceptual model of a site. It is not recommended, however, that the range of historical water table fluctuation be used to infer the vertical limits of the smear zone. Usually, this range tends to underestimate actual smear zone thickness, since the extreme fluctuations in water table elevation are seldom measured. It should also be noted that there are occasional sites at which LNAPL was released: a) from a point, such as a pipeline or tank, located below the lowest recorded elevation of the water table; or b) from a point above the groundwater low, but under enough pressure to force it downward beneath a confining layer to depths as much as several meters below the groundwater low. In either case, the zone of LNAPL contamination would extend below what might otherwise be expected. Instead of reliance on hydrographic data, direct and indirect NAPL measurement approaches should be used. Soil sample headspace data collected during drilling, which are qualitative, have been found more useful than hydrographs in most cases. Delineation of the smear zone can be supported by various field investigation methods to be described in Chapter 3; more detailed delineation can be made by collecting continuous soil cores and subjecting them to appropriate contaminant analysis. Unless the remedial goal is defined only in terms of reducing apparent product thickness, it is the entire smear zone rather than simply the zone of floating LNAPL that deserves consideration and delineation.

(3) The Problem with the Smear Zone. As stated in [paragraph 2-3d\(2\)](#) above, the smear zone is at the same time a crucial target zone for vapor extraction-based remediation of LNAPL contamination, and a zone with no or minimal air permeability. The air permeability limitation stems from the fact that the lower reaches of the smear zone are below the water table, while the upper reaches generally coincide with the wet-season position of the capillary fringe. We define the *capillary fringe* as the zone just above the water table where the capillary pressure is less than the air entry pressure, i.e., the zone that is saturated but under a gauge pressure less than atmospheric. Pores within the capillary fringe, although above the water table, are water and/or NAPL saturated. Consequently, this zone will have an air permeability value

approaching zero, unless air is sparged from beneath, the soil is drained by lowering the water table or through vacuum dewatering, or the water is driven off by heating. The applicability of these methods is discussed in [paragraph 3-8](#).

(4) NAPL Drainage. Recovery of NAPL (either LNAPL or DNAPL) from the subsurface is often accomplished by providing wells or trenches into which it can drain, as described in [paragraph 2-3c\(1\)](#) above. Such wells or trenches are positioned below the water table somewhat, so that groundwater may be drawn down by pumping, and so that NAPL in the surrounding formation can then be recovered from the well or trench (Sale and Applegate 1997). Whether as a result of active drawdown or a seasonal decline in the water table elevation, however, LNAPL that collects at the water table in excess of S_{or} cannot drain into a well or trench pipe that is at atmospheric pressure, unless the LNAPL exists in the formation at a positive gauge pressure, i.e., a pressure greater than atmospheric. Thus, neither water nor LNAPL can drain from the capillary fringe, where they exist at negative gauge pressure, into a pipe that contains air at atmospheric pressure. Only if a vacuum were exerted on the pipe, sufficient to overcome the capillary forces holding the liquid in the soil, could the liquid begin to flow into the pipe and be recovered; we term this process vacuum-enhanced recovery rather than drainage.

c. Preferential Flow.

(1) Types of Preferential Flow. Fluids do not always infiltrate through the soil uniformly, but may show preference for certain pathways, while bypassing to a great extent adjacent regions. Preferential flow is of two general types: a) flow through recognizable morphological features such as macropores or high permeability zones, and b) unstable (i.e., fingered) flow in the absence of such features. Macropores in the context of (a) are continuous non-capillary voids such as structural cracks, decayed root channels, worm channels and burrows of larger animals (Bouma 1981; Beven 1991). To this list may be added channels created through human activities, including the coarse aggregate (e.g., gravel) often placed beneath structures, around underground storage tanks, or surrounding buried utility lines, and interconnected voids present in poorly compacted fill material. Zones of locally high permeability containing smaller capillary sized pores such as sand layers can also support a kind of morphologically related preferential flow. Fingered flow refers to the instability of immiscible displacements under certain conditions, even where there are no apparent structural channels or heterogeneity at the macroscale (Hillel 1987; Kueper and Frind 1988; Baker and Hillel 1991).

(2) Preferential Flow of NAPL. It is important to appreciate that when a substantial volume of NAPL is released within a short amount of time, it has a tendency to flow preferentially within any macropores, man-made pathways, and larger fractures within fractured bedrock that it encounters during its infiltration into heterogeneous soils. These macropores represent paths of least resistance for NAPL flow when NAPL is released under a positive gauge pressure because they are the most transmissive flow paths available. Because of macropore flow, LNAPL can infiltrate over considerable distances in the unsaturated zone within a relatively short period. Even in the absence of macropores and under conditions of slow, drip release, NAPL can infiltrate to surprising depths, as illustrated in Fig. 3-3 for a DNAPL release (Poulsen and Keuper 1992). Unlike LNAPL, DNAPL can infiltrate within the saturated zone as well. This behavior has obvious ramifications with respect to the installation of soil borings, wells and other potential conduits for DNAPL transport – care must be taken to avoid vertical spreading of the source of contamination while attempting to investigate its nature and extent and during remedial efforts.

Applicable techniques to minimize these collateral effects are presented in Chapter 3.

(3) Preferential Flow of Soil Gas. Gas is typically a nonwetting fluid relative to both NAPL and water. Therefore, it too is subject to preferential flow through macropores and other preferred pathways, especially during operation of an air-based remediation technology such as SVE, IAS, or MPE. For discussions of these effects relative to SVE, refer to [EM1110-1-4001](#), Soil Vapor Extraction and Bioventing, and for IAS see [EM1110-1-4005](#), In-Situ Air Sparging. Consideration of preferential flow of gas during MPE is considered in paragraph 2-5e(5)(a). In addition, most VOCs are quite heavy compared to the average molecular weight of air. Therefore, their saturated vapors can migrate preferentially within the unsaturated zone via density-driven flow (Mendoza and McAlary 1990).

d. Multiphase Flow of Water, Air, and NAPL.

(1) Fluid flow in porous media is normally laminar; that is, it occurs at velocities that are well below the threshold for turbulent flow. Under such conditions, flow may be described by Darcy's law, which underlies much of groundwater hydrogeology. Darcy's law is also applicable to gas flow, as presented in [EM 1110-1-4001](#), Soil Vapor Extraction and Bioventing, Chapter 2, and may be further generalized to describe the movement of NAPL, water and air in porous media. The general form of Darcy's law for any phase p (for water, $p = w$; for hydrocarbon, $p = o$; and for air, $p = a$) may be written (Parker 1989; USEPA 1996; Parker et al. 1996) as:

$$q_{pi} = -\frac{k_{rp}k_{ij}}{\eta_p} \left[\left(\frac{\partial P_p}{\partial x_j} \right) + \rho_p g e_j \right] \quad [2-8]$$

where:

i, j = direction indices ($i, j = 1, 2, 3$) with repeated values indicating summation in tensor notation, x_i (or x_j) is the i th (or j th) Cartesian coordinate

q_{pi} = volumetric flux of fluid phase p in the i direction [$L^3 L^{-2} T^{-1} = L T^{-1}$]

k_{rp} = relative permeability of the porous medium to phase p [-]

k_{ij} = intrinsic permeability tensor of the porous medium [L^2]

η_p = p -phase dynamic viscosity [$ML^{-1}T^{-1}$]

P_p = p -phase pressure [$ML^{-1}T^{-2}$]

ρ_p = density of phase p [ML^{-3}]

g = gravitational acceleration [LT^{-2}] and

$e_j = \partial z / \partial x_j$ is the j component of a unit gravitational vector where z is elevation (+ upward) [-].

[Symbols in square brackets are dimensions: M = mass; L = length; T = time; and - = dimensionless.] Equation 2-8 is the commonly employed form of Darcy's law in petroleum reservoir engineering. Note that the $\partial P_p / \partial x_j$ term is the pressure gradient, while the $\rho_p g e_j$ term is the gravity gradient. Together they comprise the gradient of total hydraulic head that is the driving force for flow.

(2) In groundwater hydrology, it is more common to utilize water-height equivalent heads, rather than pressures, and the equation may be written (Parker 1989; USEPA 1996b) as

$$q_{pi} = -\left(\frac{k_{rp} K_{swij}}{\eta_{rp}}\right) \left[\left(\frac{\partial h_p}{\partial x_j}\right) + \rho_{rp} e_j \right] \quad [2-9]$$

in which:

$K_{swij} = k_{ij} \rho_w g / \eta_w$, the saturated conductivity for water [LT^{-1}]

$\eta_{rp} = \eta_p / \eta_w$, the relative viscosity of phase p to that of water [-]

$h_p = P_p / g \rho_p$, the water-equivalent pressure head of phase p [L], and

$\rho_{rp} = \rho_p / \rho_w$, the specific gravity of phase p [-].

(3) The generalized Darcy's law describes the flow of water, NAPL, and air in soils when one, two, or three phases coexist within the pore space. The equation states that the flow of a fluid p through a porous medium is in response to, and in the direction of, the driving forces, which are a negative gradient of pressure head and gravity; moreover, the rate of movement is directly proportional to the relative permeability and inversely proportional to the fluid viscosity. Each phase moves with respect to the sum of its individual pressure head gradient, $\partial h_p / \partial x_j$, and gravitational head gradient, $\rho_{rp} e_j$. Since the volumetric flux of fluid phase p is the product of the total head gradient and the relative permeability, the flux can be manipulated during MPE through the application of vacuum at the well. The higher the vacuum applied, the greater the rate at which a system will produce phase p , all other things being equal. Increasing the vacuum applied may not directly result in increased NAPL recovery, however, if increasing the vacuum results in desaturation (with respect to NAPL) of a portion of the zone through which the NAPL must flow to reach the well.

(4) Relative permeability, k_{rp} , is a coefficient reflecting the ability of a fluid to move through pore spaces that are partially occupied by other fluid(s). When phase p fluid completely fills interconnected pore spaces, the relative permeability for the p phase is 1.0; and when no mobile phase p is

present (i.e., the pores containing phase p are no longer interconnected), the relative permeability for p phase is 0.0 (Parker et al. 1996). Relative permeability is thus a function of saturation, $k_{rp}(S_p)$, and as saturation in turn depends on h_c , so too does relative permeability, i.e., $k_{rp}(h_c)$. Although the exact values of these functions may not be available at a given site, the concepts presented in [paragraph 2-4a\(3\)](#) nevertheless help one to understand what phase or phases may be present at a given location in the subsurface, which has a strong bearing on the qualitative degree to which the medium will be conductive to the various phases. In addition, it is important to note that the transport coefficient in Equations 2-8 and 2-9 is the product of relative permeability and saturated hydraulic conductivity, so the order of magnitude of the K_{sw} term has as great a significance to multiphase flow as it does to single-phase flow.

(5) Assumptions Underlying Darcy's Law. One assumption underlying Equations 2-8 and 2-9 is that the flow of phase p is not directly affected by pressure gradients in other phases. Parker (1989) notes that this assumption does not always hold, since it requires that slippage zones at phase interfaces be thin in comparison to the total film thickness of the phases. This requirement will not be met in fine-grained materials and at low values of liquid saturation, but at the same time in such cases relative permeabilities would be extremely low, so associated errors would probably not be significant. This assumption also is violated when dealing with a fluid phase that is not continuous, and through which a pressure gradient is therefore not transmitted. Such a phase cannot undergo Darcian flow, although the remaining phases are still amenable to it, so long as they are continuous. A second assumption relates to the concept of intrinsic permeability and its separation of fluid-dependent and porous medium-dependent effects on fluid flow (Parker 1989). Again, in cases of fine-grained materials this assumption may not hold, because the intrinsic permeabilities of such materials can increase by orders of magnitude when they are saturated with non-polar liquids as compared with water. Finally, the equations both treat intrinsic permeability as a tensor, while relative permeability is regarded, mainly for simplicity, as a scalar. There is evidence, however, that relative permeability itself varies with direction in anisotropic porous media, with the degree of anisotropy being strongly dependent on the fluid saturation (Kueper and Frind 1991).

(6) Continuity Equations. To model a multiphase system, a continuity equation must be written for each phase. Such equations require that mass be conserved within each phase, so that within a fixed soil volume, the change of mass within a phase equals the difference between the mass entering the volume and the mass leaving the volume, plus or minus any interphase transfer that may occur. If we assume that the fluid and medium are incompressible (not mandatory assumptions but convenient ones), the fluid phase relations (Parker 1989; USEPA 1996a) are of the form:

$$n\left(\frac{\partial \rho_p S_p}{\partial t}\right) = -\left(\frac{\partial \rho_p q_{pi}}{\partial x_j}\right) + \gamma_p \quad [2-10]$$

where: n = porosity [-],

t = time [T] and

γ_p = source-sink term incorporating transfer of mass between phases [$ML^{-3}T^{-1}$].

The source-sink terms could be particularly significant during MPE because of some of the accompanying processes (e.g., volatilization of NAPL; biodegradation of hydrocarbons).

(7) Governing Equations for Multiphase Flow. Substituting Darcy's equation for q_p (Equation 2-9) into Equation 2-10 yields:

$$n\left(\frac{\partial \rho_p S_p}{\partial t}\right) = \left\{ \frac{\partial \rho_p k_{rp} K_{swij} (\eta_{rp})^{-1}}{\partial x_j} \right\} \left[\left(\frac{\partial h_p}{\partial x_j} \right) + \rho_{rp} e_j \right] + \gamma_p \quad [2-11]$$

Therefore, we arrive at the following basic set of governing equations for the flow of water, air and NAPL phases, respectively:

$$n\left(\frac{\partial \rho_w S_w}{\partial t}\right) = \left\{ \frac{\partial \rho_w k_{rw} K_{swij} (\eta_{rw})^{-1}}{\partial x_j} \right\} \left[\left(\frac{\partial h_w}{\partial x_j} \right) + \rho_{rw} e_j \right] + \gamma_w \quad [2-12a]$$

$$n\left(\frac{\partial \rho_a S_a}{\partial t}\right) = \left\{ \frac{\partial \rho_a k_{ra} K_{saij} (\eta_{ra})^{-1}}{\partial x_j} \right\} \left[\left(\frac{\partial h_a}{\partial x_j} \right) + \rho_{ra} e_j \right] + \gamma_a \quad [2-12b]$$

$$n\left(\frac{\partial \rho_o S_o}{\partial t}\right) = \left\{ \frac{\partial \rho_o k_{ro} K_{soij} (\eta_{ro})^{-1}}{\partial x_j} \right\} \left[\left(\frac{\partial h_o}{\partial x_j} \right) + \rho_{ro} e_j \right] + \gamma_o \quad [2-12c]$$

As discussed by Parker (1989), Equation 2-12 comprises a system of coupled partial differential equations because of the dependence of the saturation, permeability and capillary head terms in each equation on their respective terms in the other equations, subject to the constraint of Equation 2-2. This system of equations may be simplified if, for example, only two of the phases are present, in which case the equation for the other phase may be disregarded. Furthermore, if a gas phase is present but there is gas phase continuity throughout the unsaturated zone such that the gas phase may also be considered to be at a nearly constant atmospheric pressure, the gas phase equation may also be eliminated. This simplification would not be justified with MPE, however, during which the prevailing gas phase pressure within the zone of influence is subatmospheric.

(8) In order to model multiphase flow using these equations, the following must be specified: the porosity and intrinsic permeability of the porous medium (or the porosity plus the saturated conductivity of each phase); the density and viscosity of each phase at a reference state; and the functional relationships among fluid saturations, capillary heads, and relative permeabilities (Parker 1989). Several of these parameters are discussed in the following paragraphs. Additional discussion of the application of modeling to MPE is provided in [paragraph 5-4](#).

e. Transport Parameters.

(1) Density. Density, ρ_p is a property of the specific fluid under consideration, and varies significantly for different organic compounds (Table

2-2). Note that the compounds or products in Table 2-2 that are less dense than water (LNAPL) are benzene, o-xylene, automotive gasoline and kerosene, while those that are denser than water (DNAPL) are trichloroethene and tetrachloroethene. Note that although density varies with temperature, density will not be affected significantly by changes in temperature over the range commonly encountered in MPE (280 to 295 °K). For comparison, the density of dry air at standard temperature and pressure (STP: 273.15 °K (0 °C) and 760 mm Hg pressure) is $1.2929 \times 10^{-3} \text{ Mg m}^{-3}$ ($1.2929 \times 10^{-3} \text{ g cm}^{-3}$; $8.0699 \times 10^{-2} \text{ lb. ft}^{-3}$), while the density of water at STP is $0.99987 \text{ Mg m}^{-3}$. Standard pressure of 760 mm Hg is equivalent to 1 atmosphere 101.35 kPa, and 14.6960 lb/in² absolute (psia).

TABLE 2-2
Physical Properties of Selected Compounds*

Compound	Density (g/cm ³)	Dynamic Viscosity (cp)	Interfacial Tension (with Air) (dynes/cm)	Interfacial Tension (NAPL-Water) (dynes/cm)	Water Solubility (mg/l)	Henry's Law Constant (atm•m ³ /mol)
Water	0.998 ⁽¹⁾	1.14 ⁽¹⁾	72.0	---	---	---
Benzene	0.876	0.647	28.85	35.0	1780	5.5E-3 ⁽²⁾
o-xylene	0.880 ⁽²⁾	0.802	30.04	36.1	170	5.4E-3 ⁽²⁾
Trichloroethene	1.464	0.570	29.5	34.5	1100 ⁽²⁾	1.0E-2 ⁽²⁾
Tetrachloroethene	1.623	0.87	31.74	47.5	150	2.3E-2
Common Petroleum Products						
Automotive gasoline	0.731 ⁽³⁾	0.48	20.5 ⁽³⁾	22.9 ⁽³⁾	---	---
Kerosene	0.807 ⁽³⁾	1.73	26.8	38.6 ⁽³⁾	---	---

*Values are given at 20° C unless noted.

⁽¹⁾Value is at 15° C.

⁽²⁾Value is at 25° C.

⁽³⁾Value is at 22-24° C.

Sources: Arthur D. Little, Inc. 1987; Demond 1988; Heath et al. 1993; Huling and Weaver 1991; Newell et al. 1995; Weast 1985; Wilson et al. 1989.

(2) Viscosity. As with density, viscosity, η , is a property of the specific fluid under consideration, and varies significantly for different organic compounds and products (Table 2-2). Note that although viscosity varies with temperature, viscosity also will not be affected significantly by changes in temperature over the range commonly encountered in MPE (280 to 295 °K). For comparison, the viscosity of air at STP is $1.71 \times 10^{-5} \text{ newton}\cdot\text{s m}^{-2}$, which is equivalent to $1.71 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1}$ and 1.71×10^{-2} centipoise (cp). The viscosity of water at STP is $1.787 \times 10^{-3} \text{ newton}\cdot\text{s m}^{-2}$, which is equivalent to $1.787 \times 10^{-2} \text{ g cm}^{-1} \text{ s}^{-1}$ and 1.787 cp, while the viscosity of water at 283 °K (10 °C) is 1.307 cp.

(3) Interfacial Tension. The surface tension at the interface between two fluids is known as the interfacial tension, σ . Because the molecules of NAPL compounds are usually nonpolar, they interact weakly with each other in comparison with individual water molecules. As a result, they exhibit interfacial tensions with air that are much smaller than the surface tension of water. Surface tension is not strongly dependent on temperature, but varies inversely with it, with the surface tension of water against air being 75.6

dynes/cm (equivalent to 75.6 g s^{-2}) at $273 \text{ }^{\circ}\text{K}$ ($0 \text{ }^{\circ}\text{C}$), 74.22 dynes/cm at $283 \text{ }^{\circ}\text{K}$, and 72.75 dynes/cm at $293 \text{ }^{\circ}\text{K}$.

(4) Wettability. The wetting angle, α (or contact angle), is the angle that a fluid assumes at an interface with a solid surface. A simple two-phase example is that of a drop of liquid placed on a dry horizontal solid surface. The drop will spread out over the surface until it comes to rest, its interface with the solid forming a characteristic contact angle that is complementary to the angle formed by its interface with the gas. Figure 2-11a illustrates the contact angle for such a drop (after Hillel 1998, Figure 2-10). A surface would be considered to be completely wetting, with a contact angle of zero, if the drop shown in Figure 2-11a were to completely flatten out. By contrast, a surface would be considered nonwetting, with a contact angle of 180° , if the drop were to remain spherical without spreading at all. If the latter drop consisted of water, such a surface would be termed hydrophobic or water repellent. Surfaces that have been exposed to hydrocarbons or organic matter and to which a sufficient quantity of organic compounds have become sorbed can become hydrophobic and oleophilic, i.e., wetting with respect to NAPL and nonwetting with respect to water (Parker 1989). Soil that behaves in this fashion still adheres to the typical concepts presented in [paragraph 2-4a\(3\)](#). Since the tangent to the interface is always drawn through the wetting fluid, Equation 2-5 still holds, but the fluids simply switch roles. Figure 2-11b depicts a hypothetical pore or fracture cross-section with two liquid phases and a gas, comprising a three-phase system consisting of water, NAPL and air (USEPA 1996b). If the solid walls of the pore are wetting, as is usually the case, the inner of the two liquids will be water. If the solid were nonwetting, however, the position of the two liquids would be reversed. The behavior of NAPL in nonwetting soils is a subject of current research.

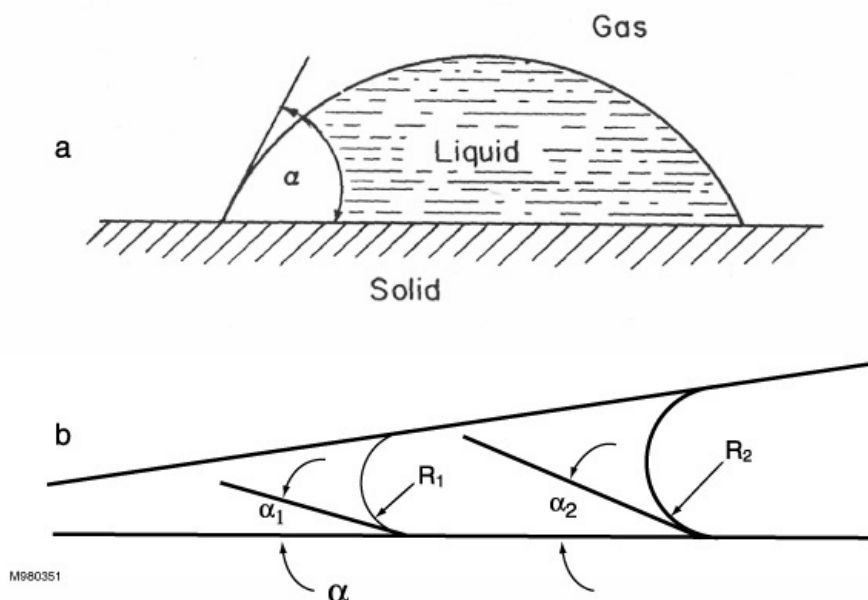


Figure 2-11. a) The contact angle of a drop resting upon a plane solid surface (Hillel 1998); b) Hypothetical pore cross section with two fluids. α is the contact angle; R is the radius of curvature. (USEPA 1996b)

2-5. Response of NAPL, Water, and Air to Vacuum.

a. Nature of the Problem. MPE works by applying a vacuum to the soil (usually via an extraction well), and by providing means for gas, water and NAPL, if present, that arrive at the well to be removed from it and handled aboveground. Its effectiveness is governed by the degree to which the process exerts its effects throughout the zone targeted for cleanup. The subsurface effects caused by application of a vacuum to the soil are not simple, however, nor are they obvious. Nor, for that matter, is the fluid flow behavior within the conveyance piping leading to the aboveground system obvious. The majority of MPE systems that have been operated have been monitored by measuring integrated parameters that can be measured aboveground, such as the flow, pressure (vacuum), temperature, and contaminant concentrations of the extracted stream(s), and the volume(s) of liquids recovered. Data have also typically been collected at monitoring wells screened over a wide (e.g., > 3 m) depth interval, including groundwater and LNAPL elevations, and at times, concentrations of contaminants (and/or other geochemical parameters) in groundwater. Less often, data have also been collected from discrete monitoring points, including pressure (vacuum) influence and O_2 , CO_2 , CH_4 and contaminant concentrations in soil gas; however, consistent approaches to the interpretation of such data are not available. Until recently, very little data have been published shedding light on the following questions: What portions of the subsurface are affected by MPE? Does MPE cause desaturation of soils near the extraction well? What is the zone of influence of an MPE system, and how does it correspond to the zone of influence of, for example, SVE systems? What conditions give rise to efficient modes of multiphase flow within the conveyance piping? Under what conditions does MPE work effectively? Postulated answers have, so far, often substituted where real data have been absent. One of the purposes of this EM is to provide a basis so that these questions can begin to be addressed more directly. This basis will incorporate theory, observations, and recently available data.

b. Effects at the Point of Vacuum Application. When a straw is placed below a free water surface and suction is applied, liquid flows up the straw in response to the imposed pressure gradient. Everyone who has sipped a beverage through a straw has direct experience with this process. When the liquid level drops to the bottom of the container, a combination of liquid and air is briefly drawn into the straw - a simple example of MPE. After the available liquid has been suctioned off, if suction were to continue to be applied, air alone would be drawn into the straw. Turning now to subsurface applications, this stage of the process is analogous to SVE: application of a vacuum to a well screened within the unsaturated zone will produce a flow of gas, again in response to the imposed pressure gradient. The greater the vacuum applied, the larger the imposed pressure gradient. The resulting volumetric flux of fluid is a function of the pressure gradient, diameter of the pipe, pipe roughness and associated frictional losses for the pipe and fittings, and the rate at which the subsurface porous media can yield gas. In all but the most permeable subsurface applications, the subsurface, and not the capacities of the aboveground components, limits the resulting volumetric flux.

c. Effects Within the Extraction Well During Extraction of Gas Only. To a first approximation, the magnitude of vacuum measured within an appropriately sized well (i.e., as indicated by a vacuum gauge tapped into the well head) will be the same as the vacuum exerted at all portions of the well screen above the liquid level. The groundwater elevation within a well or trench will also respond to the applied vacuum, with the height of upwelling being equal, at equilibrium, to the vacuum applied expressed as a water-height equivalent head

(Johnson et al. 1990; USEPA 1991a). Because the height of upwelling reflects a balance of forces between the applied vacuum and gravity, a submerged pressure transducer placed within the well and referenced to atmospheric pressure will register no change in head, i.e., upwelling in response to vacuum does not constitute a change in the piezometric surface. Less well appreciated is the fact that the capillary fringe (defined in [paragraph 2-4b\(3\)](#)) also will translate upward in response to the applied vacuum. This can occur to the point that previously unsaturated soil, even the soil surrounding the filter pack/well screen, can become inundated, blocking airflow to the well. The phenomenon of upwelling is discussed at greater length in [EM 1110-1-4001](#), Soil Vapor Extraction and Bioventing, Chapter 3, Site Characterization and Technology Screening, and Chapter 4, Bench- and Pilot-Scale Testing for SVE and BV. Upwelling, if uncontrolled, can result in the liquid level rising above the top of the well screen, greatly impeding or even preventing the flow of air into the well. In many applications, one of the main goals of MPE is to remove water as fast as it can enter the well, so as to enhance gas flow into the well.

d. Effects Within the Extraction Well and Piping During MPE.

(1) Extraction Well Configurations. There are several possible ways to continually remove liquid (water and/or NAPL) from a well to which a vacuum is being applied. These include: a) use of a submersible pump placed within the well to push liquid to the surface through a discharge pipe positioned inside the well casing; b) use of an aboveground vacuum pump to suction liquid out of the well through a suction pipe; and c) application to the well casing of a vacuum large enough to lift liquid to the surface. The latter is a form of well point dewatering, used in the construction industry (Powers 1992). The first two of these approaches are known as "pipe within a pipe" technologies, because the delivery tube sits inside the well casing. In either of these cases, if water is being removed as fast as it can enter the well, the water level within the well is determined by the elevation of the pump or pipe inlet. Thus, these two approaches control upwelling, leaving the well screen above the water level open to gas flow, if the formation is conducive to it. The third approach, however, essentially exacerbates upwelling, inundating the well screen with liquid lifted up within the well. If the third approach is carried out at such a rate, however, that liquid is evacuated from the well faster than it can recharge, then it too can potentially be compatible with vapor extraction. Therefore under the right circumstances, all three are potential methods of carrying out MPE. Upwelling will occur within an MPE well that is screened in part above the water table if water enters the well at a greater rate than it can be extracted from the well. This condition can occur during MPE if there is a limitation to the rate at which water can be removed from the well (relative to the rate at which it enters the well), as for example if there is insufficient airflow to lift the liquid out of the well as droplets, or insufficient suction to lift it as a solid column of water.

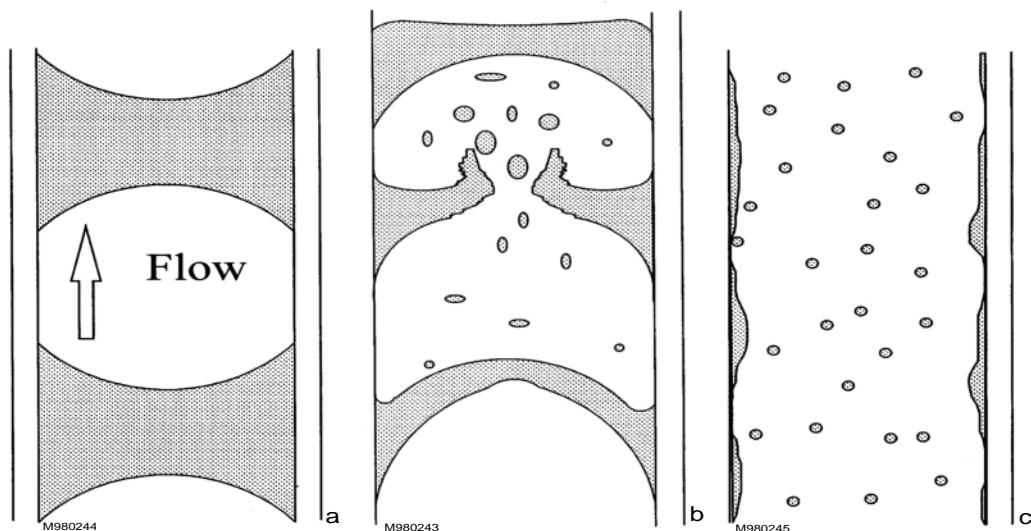
(2) MPE Flow Regimes. Three flow regimes have been identified to occur within TPE piping (Peargin 1997). The flow regime is believed to be governed by the hydraulic and pneumatic properties of the formation, and may be controlled largely by adjusting the drop tube depth and varying the air/water ratio (or air velocity) that one can achieve, e.g., by opening the atmospheric bleed valve and/or priming valve at the well head. Peargin (1997) has made the following observations concerning these flow regimes:

(a) Slug flow regime. At moderate air flow velocities, nearly equal ratios of air to liquid prevail, with liquid being lifted as continuous slugs moving at approximately the same velocity as the air (Figure 2-12a). The slugs

of liquid occupy the entire cross-sectional area of the piping, and line losses associated with slug flow (also termed transitional flow) are quite small.

(b) Churn flow regime. At somewhat higher airflow velocities, air/liquid ratios increase. Bullet-shaped Taylor bubbles break through the water slugs from below, with liquid then cascading downward to form new slugs (Figure 2-12b). The churning action of lifting and falling water slugs increases the drop tube line losses associated with churn flow. In addition, oscillations in drop tube and casing vacuums are typically observable.

(c) Annular flow regime. At higher airflow velocities, higher ratios of air to liquid prevail, with liquid being lifted in individual droplets and as an annular film along the inside surface of the piping (Figure 2-12c). The central cross-section of the pipe is open to airflow, and line losses associated with annular flow are relatively small. Of the three flow regimes, annular flow is the most preferable. Peargin (1997) believes that only the lowest permeability, highest operating vacuum settings justify use of a TPE drop tube as a cost-effective engineering decision rather than use of DPE.



- a. Slug Flow Regime:** Gas/liquid ratio nearly equal; flow rate low. Liquid lifted as continuous slug at same velocity as gas. Slug occupies entire cross-sectional area of pipe; little line loss.
- b. Churn Flow Regime:** Gas/liquid ratio and flow velocity increase. Bullet-shaped Taylor bubbles break through water slugs from below. Liquid cascades downward to form new slug. Churning action of lifting and falling water slugs increases line loss.
- c. Annular Flow Regime:** With increasing gas/liquid ratio and flow velocity, liquid is lifted in individual droplets and as annular film. Central cross section of pipe open to airflow; little line loss.

(M980244)

Figure 2-12. MPE Flow Regimes. (Peargin 1997. Reprinted by permission of T.R. Peargin, Chevron Research and Technology Corp.)

e. Effects Adjacent to the Extraction Well/Porous Media Boundary.

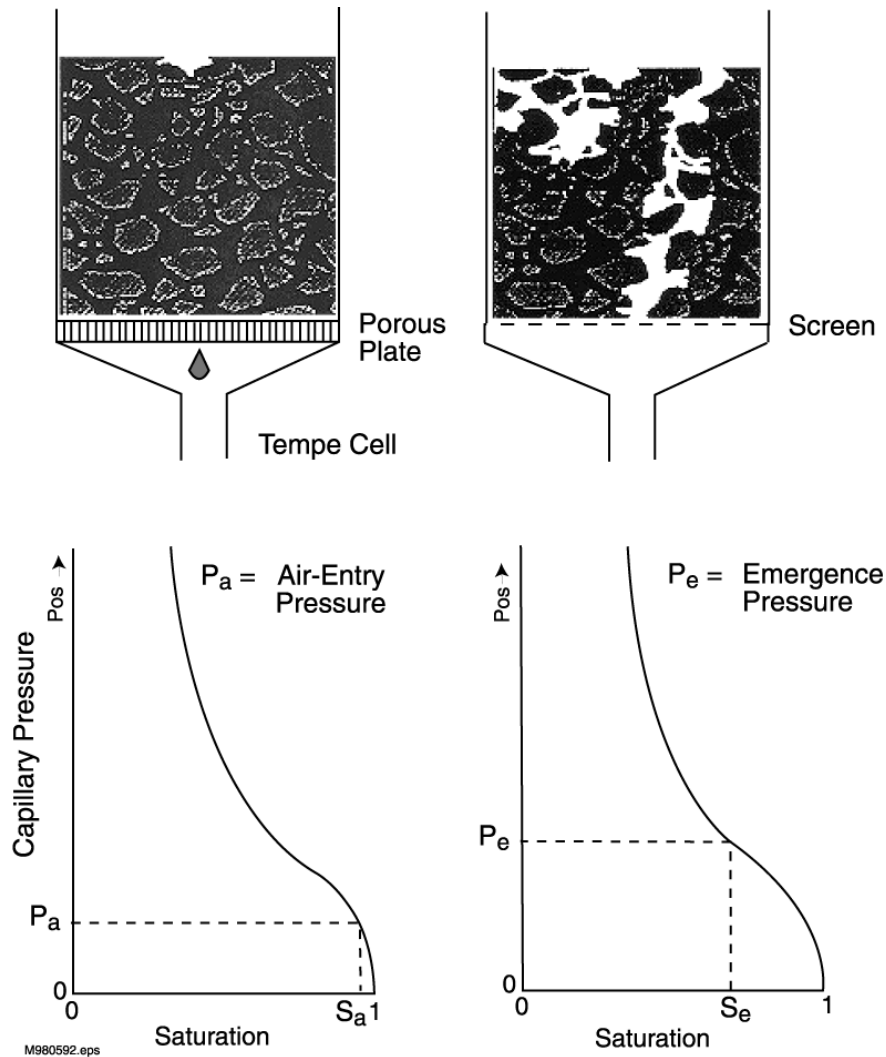
(1) General Effects. Picture the case of a straw placed in a glass containing crushed ice and beverage. When the liquid level has been drawn down to the bottom of the glass, some liquid will still remain in the pores between the pieces of ice, held there by capillary forces despite the force of gravity. Continued suction will draw in a mixture of liquid and air, resulting in the

removal of some of that retained liquid. We call this process slurping. A similar effect occurs in the neighborhood of a well screen under imposition of a vacuum, with the difference that now, as liquid is removed, more liquid flows in from the formation to take its place. If liquid is being removed as fast as it is able to discharge into the well from the formation, then the vacuum will be exerted uniformly on the exposed portion of the filter pack.

(2) Upwelling. One of the effects that occurs in response to application of vacuum, as was discussed in [paragraph 2-5c](#), is upwelling of water. The position of the water table (i.e., the piezometric surface) is, by definition, the level at which water is in equilibrium with atmospheric pressure. A reduction in the pressure of the soil air in air-filled pores that are in communication with an SVE or MPE well produces a reduction of h_c and upward movement of water into those pores, provided $h_c < h_{cwe}$, the water entry capillary head. By explanation, as a wetting front within a moist, fine-textured soil layer moves into an adjacent, dryer, coarser-textured layer, the capillary head must diminish at least to the water entry value of the coarser layer before water can begin to occupy its larger pores (Miyazaki et al. 1993). The potential height of upwelling is equal to the vacuum head exerted in the air-phase at that location. For example, if 100 cm H₂O vacuum is applied to the SVE well, the level at which soil is saturated immediately below the well will be as much as a meter higher than the pre-SVE level. Note that the position of the piezometric surface as referenced to atmospheric pressure will not change during this process, unless water is extracted at a faster rate than it can recharge. Further explanation is provided in [EM1110-1-4001](#), Soil Vapor Extraction and Bioventing, Chapter 3, Bench- and Pilot-Scale Testing for SVE and BV. The following paragraphs focus on the effects of MPE on fluids in the well filter pack and adjacent soils.

(3) Soil Moisture Retention Analysis Analogy. What happens at the filter pack (and beyond it, in the formation) can best be understood by first considering the simple case of a soil sample subjected to a laboratory soil moisture retention analysis. In this case, a Tempe cell or similar device is used, in accordance with the method of Klute (1986) or ASTM D2325. The Tempe cell is a cylindrical sample holder with a porous plate against one planar boundary (Figure 2-13). A porous plate is selected that has small enough pores so that air entry will not occur through it, even under the highest suction that will be applied to the cell any time during the test. The porous plate is first presaturated with deaerated water, and a saturated soil sample is placed in contact with it. The porous plate serves, in effect, as a capillary barrier that will prevent airflow from being able to occur through the soil sample. A subatmospheric pressure, P_{sub} , is now applied to the porous plate/test cell assembly in a stepwise fashion, i.e., we make the water pressure more negative relative to the gas phase above the sample, which remains at atmospheric pressure, P_{atm} . By Equation 2-3, a reduction in the wetting pressure, P_w , results in a commensurate increase in the capillary pressure, P_c , within the sample. As P_c increases, there comes a point at which the air-water interfaces on the upper boundary of the soil sample (the boundary opposite the porous plate) achieve a radius of curvature that is smaller than the largest pore open to the atmosphere, and air enters the sample (Parker 1989). We term this point the air-entry pressure, P_a (Figure 2-13), or equivalently, the air entry capillary head, h_{cae} , defined as the lowest capillary head value that a soil can have at which air begins to displace water from the soil's largest pores. As the capillary pressure is increased further, the radius of curvature of the interface decreases further, and more air progressively enters the sample. In this manner, the wetting phase (water) will be progressively displaced from larger pores by the nonwetting phase (air), such that at each increasingly larger value of P_{sub} , an incremental fraction, n_a , of the porosity of the soil will become air-filled. As long as the h_{cae} value of the porous plate is not exceeded, this process can proceed, with water being displaced from smaller and

smaller pores until the soil sample is quite dry. The resulting set of points, $P_c(S_v)$ (Figure 2-14) describes the draining capillary pressure-saturation curve for the sample. This process of displacing water by air, through application of suction, is analogous to what occurs during MPE.



Air-entry pressure versus air emergence pressure. Tempe cell apparatus (upper left) has a porous plate that serves as a capillary barrier preventing air flow. Step-wise application of suction to the initially saturated cell across the porous plate induces gradual desaturation, yielding the soil's capillary pressure-saturation curve (lower left and right). The capillary pressure that result in the first displacement of water by air at the upper boundary of the soil sample (upper left) is the air-entry pressure, P_a . By contrast, the air emergence pressure, P_e (i.e., capillary pressure at which air is first able to emerge through a soil not bounded by a porous plate (upper right) occurs at the inflection point of a van Genuchten (1980) curve fitted to the capillary pressure-saturation data (lower right). (White et al. 1972; Baker and Groher 1998)

Figure 2-13. Air-Entry Pressure versus Air Emergence Pressure. (White et al. 1972; Baker and Groher 1998. Reprinted by permission of Battelle Press. Copyright 1998. All rights reserved.)

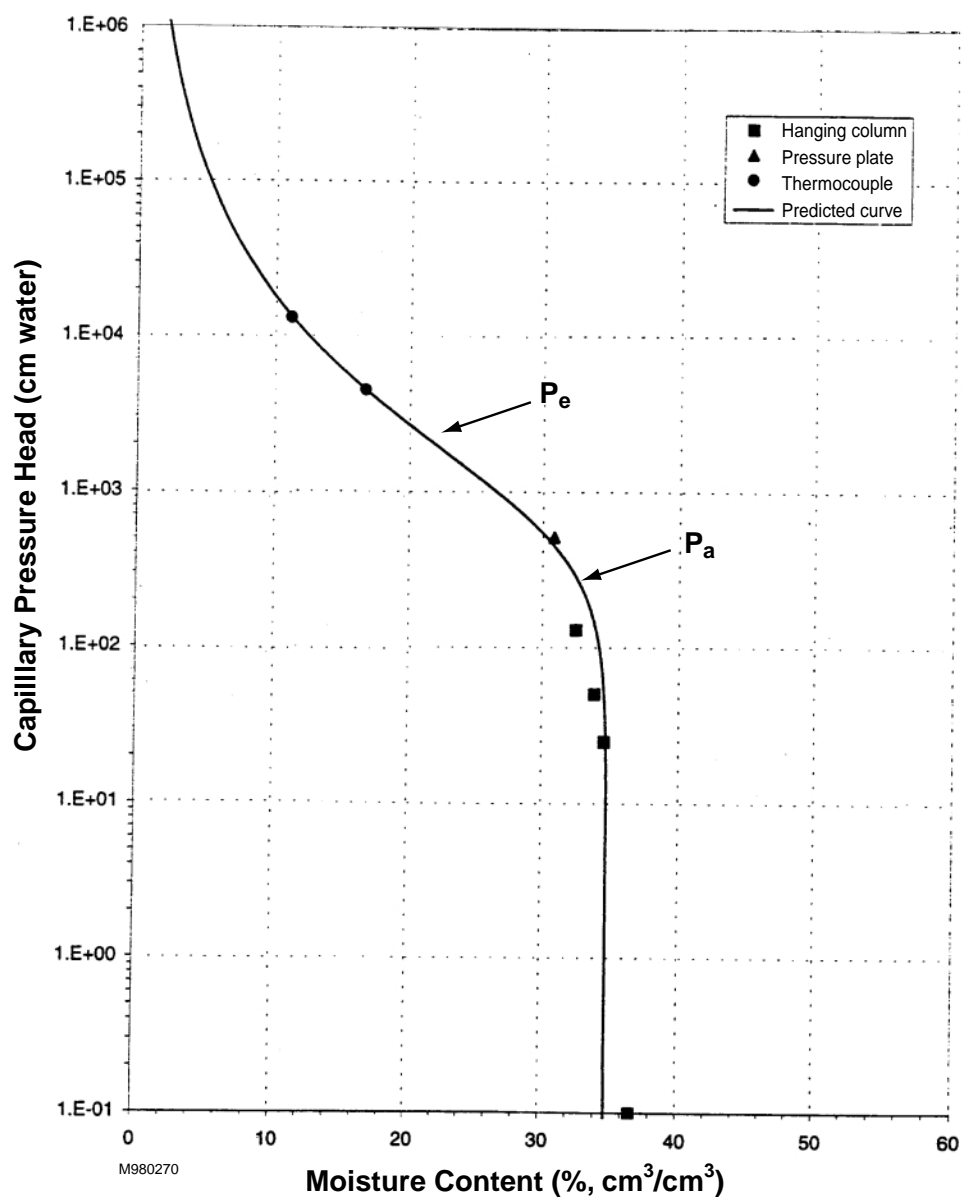


Figure 2-14. Predicted Water Retention Curve and Data Points for a Silt Loam. P_e = Air emergence pressure; P_a = Air entry pressure.

(4) Well Filter Pack. In the case of a well filter pack subjected to vacuum, as P_{sub} is applied, air is free to enter the filter pack at its value of P_a . Because of the relatively narrow particle and pore size distributions of the filter sand, and because there is no corresponding capillary barrier on the vacuum side of the soil as there was with the Tempe cell, air can displace water from most of the larger pores of the filter pack at the air emergence pressure, P_e , that is not much in excess of P_a , and the filter pack will permit air to flow readily through it. All filter pack gradations in conventional use have small enough values of P_e to be readily drained during MPE.

(5) Formations Adjacent to the Well. As vacuum propagates from the well out into the formation, a pressure gradient is established that is the driving force for fluid flow toward the well. Whether flow of NAPL, water and/or air is induced through the formation and into the well depends on a number of factors: the vacuum imposed, the saturation of each fluid and the history of saturation, the pore sizes occupied by each fluid, the associated permeabilities of the various available pathways, and the fluid properties (e.g., density, viscosity). The equilibrium vacuum experienced in the well will both be a function of vacuum imposed by the pump and the flow rate of fluids within and hence into the well. Consider two cases using the same pump: in one case, the well screen is blocked and no flow occurs, then the vacuum experienced in the well rises to its maximum value; in the case of a completely unblocked (and unimpeded) screen drawing only air into the well, the flow rate of air in the well reaches its maximum value, and the vacuum experienced/measured in the well will be at a minimum. The behavior of the formation therefore affects the vacuum that can be applied at the well, with the effect that the vacuum experienced in the formation may change over time. In practice, maintaining a prescribed flux or pressure boundary condition cannot be selected *a priori* in the absence of site-specific data. To simplify what is in fact a very complex set of interactions, we shall consider: a) a uniform, homogeneous formation; then b) a layered case; and finally c) a more heterogeneous situation. If the adjacent formation is uniform and homogeneous, its behavior depends largely on its initial saturation and capillary pressure-saturation curve. Let us assume that the screen interval of the MPE well spans the water table, and that the inlet of the TPE drop tube or inlet pipe is also situated at the pre-extraction water table.

(a) Uniform, homogeneous formations.

- If the formation is quite permeable (e.g., a fine- or medium-textured sand) and has a relatively thin capillary fringe (e.g., <25 cm), imposition of a vacuum will readily pull water into the well. LNAPL also may enter the well, but only if it occupies an interconnected volume of adjacent pores. Gas may be prevented from entering the well by flooding of the inlet tube with liquid from this relatively transmissive formation. Sliding the inlet of the drop tube up above the water table can "break suction" allowing air into the tube, but in this type of formation it can be difficult to position the drop tube so as to maintain a mixture of liquid and air, because with only a slight upward repositioning of the tube, air rather than a mixture of air and liquid will be extracted. This type of setting is in general too transmissive for TPE, and may be better suited for separate vacuum extraction and liquid pumping, i.e., DPE (Peargin et al. 1997). Figure 2-15a nevertheless depicts what occurs when TPE is applied within such a setting.

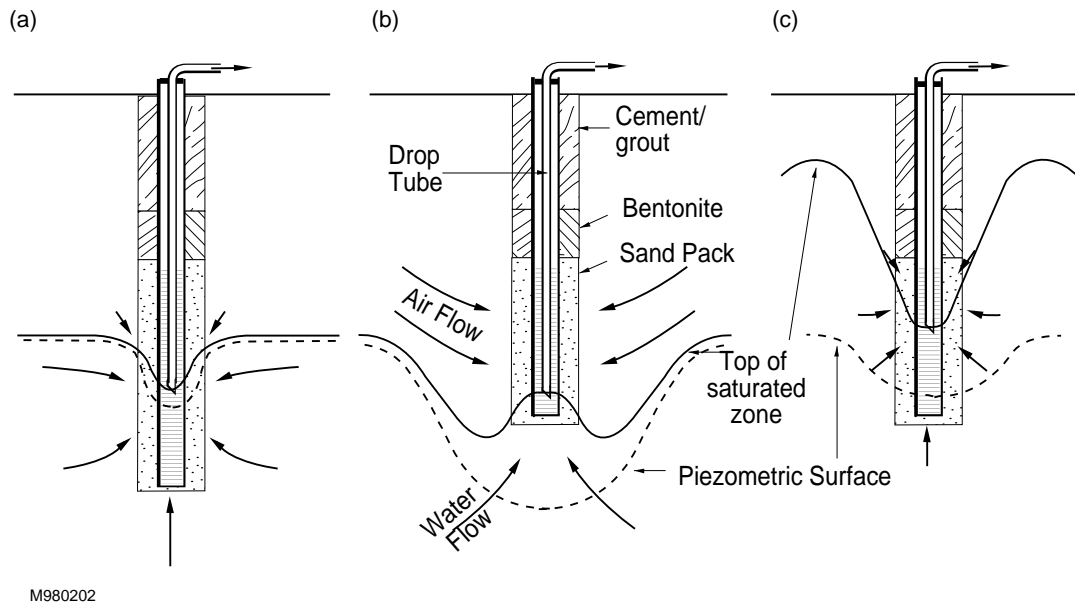


Figure 2-15. Hypothetical scenarios that can prevail during MPE. Length of arrows indicates fluid velocity; Dashed lines indicate piezometric surface; solid curve indicates top of saturated zone (top of capillary fringe within the formation). a) In high permeability settings, drop tubes can be flooded by water. b) In moderate permeability settings, a desirable ratio of gas; liquid can be extracted, leading to the desired enhancement of gas and/or liquid flow. c) In low permeability settings, it may not be possible to induce a significant amount of gas flow from the formation into the well. Only (b) is desirable. (After Baker and Groher 1998. Reprinted by permission of Battelle Press. Copyright 1998. All rights reserved.)

- If the formation is moderately permeable (e.g., a very fine sand or silt) with a capillary fringe zone of moderate thickness (e.g., 25 to 250 cm), imposition of a vacuum will likely pull a combination of liquid (water and LNAPL, if it occupies interconnected adjacent pores) and air into the well. Figure 2-15b depicts application of MPE in this type of setting, which is generally well suited to MPE. The more moderate transmissivity of this type of formation means that there will be a wider depth interval over which the inlet of the drop tube can be positioned and still result in a mixture of liquid and air being extracted. In this setting some of the vadose zone soil with which the MPE well is in contact will either already be unsaturated prior to application of vacuum, or will be able to become dewatered enough to be conductive to airflow upon application of a moderate vacuum. The vacuum that will need to be applied to begin to move air through a soil can be predicted based on capillary theory. Air will begin to flow through the soil at a capillary pressure value we again term the air emergence pressure (Stonestrom and Rubin 1989), P_e , that is somewhat greater than its P_a (air entry) value, at which air could first displace water along one boundary of the soil. By contrast, P_e , at which air is first able to flow through an initially saturated porous medium, has been found to lie near the inflection point of a van Genuchten (1980) curve fitted through a set of $P_c(S_w)$ data for that medium (White et al. 1972; Baker and Groher 1998). The difference between the two points is illustrated in Figure 2-13. Thus, we would not expect to be able to dewater a soil unless we can propagate into the soil a vacuum equal to the soil's P_e value. This explains why measurements of saturation

using neutron probes in the vicinity of MPE wells have shown that in several cases, the soil was not able to be dewatered during MPE (Baker and Groher 1998). For comparison, Table 2-3 presents approximate P_c values (and the equivalent effective capillary fringe heights) for a range of soil types, based on inflection points of the family of capillary pressure-moisture content curves illustrated in Figure 2-9. Note that each textural class encompasses a range of particle-size and pore-size distributions, and hence a range of associated capillary pressure-moisture content curves; the data are merely representative.

TABLE 2-3
Approximate Air Emergence Pressure and Effective Height of
Capillary Fringe by Soil Textural Class
(based on Figure 2-9)

Soil Textural Class (USDA)	Air Emergence Pressure (cm H ₂ O)	Ht. of Capillary Fringe (m)
Sand	10	0.1
Loamy sand	10	0.1
Sandy loam	30	0.3
Loam	40	0.4
Sandy clay loam	50	0.5
Sandy clay	100	1
Clay loam	100	1
Silt loam	200	2
Silty clay loam	500	5
Clay	>2000	>20

- Towards the lower end of the moderate permeability range, as defined in the previous paragraph, and especially in deeper applications where the depth of the water table beneath the ground surface is in excess of the suction lift of water (approximately 10 m), it may be advantageous to introduce outside air into the well initially as a way of providing enough air velocity to carry entrained liquid droplets up the well or drop tube. Such methods of priming the well with air offer ways to potentially overcome the problem of the formation not initially yielding enough airflow to sustain multiphase flow of liquid out of the well.
- Another phenomenon that occurs near a vacuum extraction well, especially in formations of moderate permeability, is redistribution of vadose-zone water (Baker and Bierschenk 1995; Baker 1995). Imposition of a vacuum gradient at an MPE or SVE well reduces the value of the nonwetting capillary pressure, P_{cn} , of air-filled pores that are in communication with the well; thereby reducing the capillary pressures, P_c (see Equation 2-3), and increasing S_w accordingly. As a result, provided that the water saturation value lies within the range: $S_{wr} < S_w(P_c) < S_w(P_{cn})$, unsaturated flow of water is initiated in the direction of the MPE well. If a sufficient

volume of moisture arrives at the well, the sharp transition to the larger pores of the sand filter pack and the well screen can constitute a capillary break, and water can "pile up" within the soil around the filter pack, as has been observed using neutron probe observations during MPE (Baker and Bierschenk 1995). It follows that the capillary pressure of the soil around the filter pack cannot fall below the P_a value for the filter pack, because at that point water would begin to seep into the sand pack; consequently, the S_w value of the soil around the filter pack will remain no higher than its $S_w(P_a)$ value (Baker 1998). This redistribution of vadose-zone liquid toward the extraction well was anticipated in theory by McWhorter (1990). Although this effect would probably not be of significance in a well-drained, permeable soil, it does manifest itself in many settings through reductions in k_a and associated dramatic head losses adjacent to SVE vents, resulting in poor vent well efficiency. This aspect is discussed in [EM 1110-1-4001](#), Soil Vapor Extraction and Bioventing, Chapter 4, Bench- and Pilot-Scale Testing for SVE and BV, Well Efficiency.

- If the formation is slowly permeable (e.g., a silty-clay or finer-textured formation) with a thick capillary fringe zone (e.g., > 250 cm), imposition of a vacuum will likely result in a limited recovery of liquid and little or no gas either (Figure 2-15c). Although a higher vacuum will impart a larger gradient and, in accordance with Equations 2-8, 2-9, 2-10 and 2-11, will increase the resulting fluid flux, the much lower permeability of this kind of formation will still largely limit the flux. In addition, airflow through the soil may not be able to be initiated due to the high value of the soil's P_a . Such low permeability settings are not likely to be conducive to MPE, unless a considerable amount of contaminant mass resides in preferential pathways that do experience fluid flow during application of the vacuum (Baker and Groher 1998). This type of setting is, however, also the kind that is most susceptible to being dominated by unwanted preferential flow, such as short-circuiting of air from the surface to the well through macropores or structural cracks (see paragraph 2-4c), with limited areal vacuum influence elsewhere. Priming will be of limited benefit in such settings.

(b) Layered soils. If the MPE well screen intersects two or more soil layers of differing pore size, airflow will be initiated first in the layer with the smallest P_a value (i.e., the path of least resistance), which we shall term Layer 1. This is because unlike the case of the soil moisture analysis (paragraph 2-5e(3)), there is no capillary barrier adjacent to the MPE well screen to prevent air from entering through some pathways and not through others. If Layer 1 can produce air or liquid at a rate commensurate with the capacity of the pump and piping at a given value of applied vacuum, other layers will not be dewatered nor produce much fluid. If Layer 1 is not very permeable, however, and cannot produce as much fluid as the pump/piping system is capable of moving, the vacuum being applied will increase, and the P_a value of another soil layer, Layer 2, will be attained, allowing that layer to begin to yield air. Once again, however, if Layers 1 and 2 can produce enough fluid to satisfy the pumping system's capacity at that value of applied vacuum, other layers will not be dewatered nor produce much fluid. This process can be visualized (Figure 2-16), and will proceed until flow through conductive layers of the formation matches the capacity of the pumping system at the applied level of vacuum. The significance of an inability to dewater other layers or entire regions of the subsurface is profound, because if zones of stagnant or limited airflow are reservoirs of contamination, the primary mechanism for mass transfer through the soil matrix becomes aqueous-phase diffusion, which is extremely slow (McWhorter 1995). Thus regardless how much air may be moving

through conductive layers or scattered permeable pathways, the course of the remediation will be diffusion-limited and protracted. On the other hand, if the objectives are simply mass removal, and if leaving a substantial fraction of the contaminant mass behind in the soil matrix can be tolerated, then MPE may still be worthwhile (Baker and Groher 1998). Deciding which is the case is an important aspect of the task of setting acceptable remedial goals.

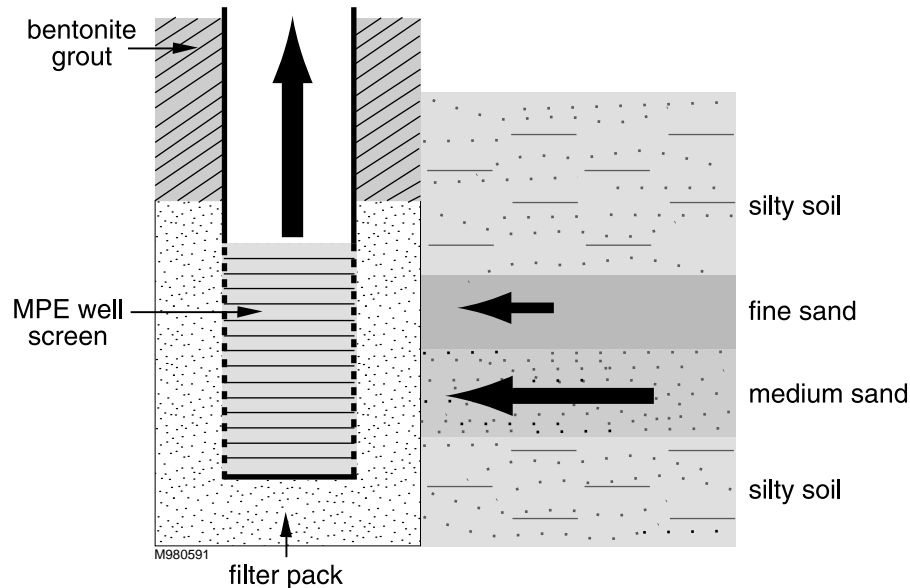


Figure 2-16. Preferential Airflow into MPE Well from a Layered Soil. Arrow sizes are proportional to airflow velocities, silty layers are not conductive to air in this case.

(c) Heterogeneous settings. If the MPE well screen is placed within a heterogeneous setting, i.e., one in which the pattern of distribution of soil types, layers or soil morphological features is not readily discerned, the response of the subsurface to application of vacuum is more difficult to characterize. Nevertheless one may expect the same sort of response as described in the preceding paragraph on layered soils, namely that flow will be predominantly along paths of least resistance. Therefore, the greatest degree of treatment will occur along preferential pathways. Whether neighboring soil (adjacent to or at a distance from conductive pathways) is treated by MPE processes depends on how great the contrast in soil properties is between the most conductive zones and less conductive zones.

f. Influence of MPE on NAPL Recovery.

(1) NAPL Saturation. If NAPL is present in the formation near an MPE well, it will flow to the well if it occupies an interconnected series of pores leading to the well. Recall that within the zone where NAPL is present, water is also present. As the wetting phase, water typically wets the soil matrix, forming a continuous phase within it (Sale and Applegate 1997). NAPL, by contrast, is typically non-wetting with respect to water, and tends to occupy the larger pore spaces. Whether or not NAPL constitutes a continuous phase within the soil depends on its saturation, S_o , and the geometry of the NAPL-filled pores. Furthermore, the transmissivity of the formation to NAPL is likewise a function of S_o , pore geometry, and the height of the continuous NAPL flow paths.

(2) Principles of NAPL Flow Path Management. As NAPL is extracted from an area within the subsurface, the NAPL saturation of that area diminishes. In the process, the height of continuous NAPL flow paths contracts, leaving behind areas of residual NAPL saturation, S_{or} , within which NAPL is immobile. Conceptually, NAPL recovery is a process of managing conditions within the NAPL flow paths to optimize NAPL flow. Quoting Sale and Applegate (1997), "the principles of flow path management dictate the importance of maintaining maximum NAPL saturations, NAPL heights, widths of NAPL flow paths, and NAPL gradients. Allowing any of these parameters to approach zero will likely limit the effectiveness of a NAPL recovery system."

(3) Effect of Vacuum on NAPL Flow Paths. Application of a vacuum during MPE will increase the head gradient driving NAPL toward the extraction well. Therefore, given a sufficiently large volume of recoverable NAPL, vacuum extraction will enhance free product recovery rates. Since MPE also inevitably enhances water recovery rates, water may displace NAPL from portions of its flow paths. Consequently, if NAPL saturations and flow paths are relatively small, application of vacuum can cause NAPL-filled pores to "snap off." Thereupon, NAPL will not be able to flow as a separate phase through those pathways again, unless the interconnections later become reestablished. These statements apply to both LNAPL and DNAPL.

(4) Recoverability. If enhanced LNAPL recovery is the objective, consideration needs to be given to evaluating the recoverability of the product. Paragraph 3-5a provides details regarding applicable methods. For example, the apparent LNAPL thickness in monitoring wells is not necessarily a good indication of the volume of recoverable product. Figure 2-17 shows the relationship between relative LNAPL transmissivity and apparent product thickness for a sandy and a silty soil (Parker et al. 1996). In cases where apparent product thickness is less than approximately 30 cm, true product thickness in the formation tends to be so small, especially in finer-textured soil, that the volume of recoverable product is negligible.

(5) LNAPL Extraction Depth. Care must also be taken to select the optimal depth of LNAPL extraction. Positioning of TPE drop tubes or DPE pump inlets so as to maintain the highest LNAPL saturation possible adjacent to the well will prolong the period before snap-off occurs. Placement of the intake device adjacent to layers of highest LNAPL transmissivity is advisable. Note that with TPE, if the drop tube is positioned above the apparent LNAPL elevation in moderate permeability soil, upwelling will occur in the soil adjacent to the well, because liquid is not being removed as fast as it redistributes upward in response to the vacuum. This upwelling in response to the application of vacuum will cause the zone of highest LNAPL saturation to translate upward along with the capillary fringe (unless a confining layer is in the way). If upwelling does occur, the optimal depth of extraction will be shallower than one would expect from pre-MPE apparent product elevations. Creating a cone of depression during MPE will not necessarily negate this effect, and can at times cause interruption of LNAPL flow paths to the well. Comparisons of LNAPL recovery obtained during sequential skimming, slurping and drawdown are provided in Table 4-8 and Figure 4-13.

2-6. Fate Mechanisms for NAPL in the Subsurface.

a. Information Sources on Fate and Properties of NAPL Constituents. A complementary discussion of fundamental fate and transport mechanisms for NAPL in the subsurface may be found in EM 1110-1-4001, Soil Vapor Extraction and Bioventing, Chapter 2. In addition, Chapter 3 lists VOCs considered amenable to SVE, and summarizes the effectiveness of SVE on general contaminant groups

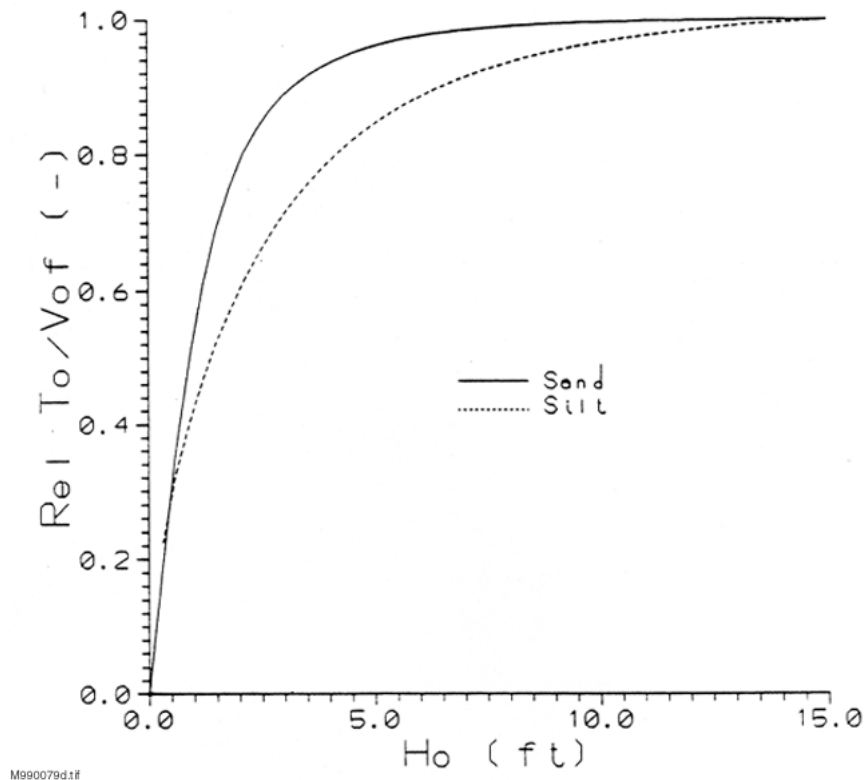


Figure 2-17. Relative Oil Mobility Versus Apparent Oil Thickness for Two Soils (EPA 1996b). To/Vof is the oil mobility factor, where To is oil specific volume. $Rel To/Vof$ is the oil mobility factor normalized by its maximum value. Ho is apparent LNAPL thickness.

for soil. These tables are also applicable to MPE. Finally, Appendix B in EM 1110-1-4001 contains useful tables of properties of common organic pollutants, including the vapor pressure, solubility, Henry's law constant, partitioning coefficient and half-life for a variety of compounds amenable to MPE.

b. Fate Mechanisms. Since MPE often addresses NAPL contamination, the following briefly reviews various NAPL fate mechanisms in soil and groundwater.

(1) Volatilization. Foremost from the standpoint of MPE is volatilization, in that a number of the compounds of potential concern in common organic liquids are VOCs that can be removed from the subsurface most readily if they can be volatilized and carried aboveground with advected air. Although some contaminants, such as acetone and ethylene glycol that are highly (or infinitely) soluble may be extracted better in the dissolved phase, most VOCs are more extractable in the gas phase, in accordance with their Henry's law constants. For that reason, obtaining a good distribution of airflow, and ensuring adequate air exchange within subsurface locations where NAPL resides, are of primary importance during MPE. The greater the surface area of NAPL exposed to volatilization, the more rapid will be the mass transfer, other factors being equal. Thus droplets of residual NAPL in a sandy vadose zone, for example, will volatilize more readily than a NAPL pool perched upon a clay lens in that same zone. Also, since various VOCs that comprise NAPL differ as to their volatility, the composition of the extracted gas will vary over the course of the remediation: higher fractions of more volatile compounds are to

be expected earlier, with less volatile compounds following later. Thus, the results of a short-term pilot study provide only an early indication of what will occur over a longer period. In addition, the concentrations of the individual VOCs present in the off-gas will very likely decline over time. As contaminant mass is removed, the concentrations remaining in the subsurface will of course decline, and the remaining composition will shift to a predominance of the less volatile compounds. Because of mass transfer limitations, it is not uncommon for these concentrations to decline asymptotically, with a substantial contaminant mass often remaining in the soil once off-gas concentrations have become asymptotic. If the contaminant concentration remaining upon reaching an asymptote is less than the remedial goal, the remediation is deemed complete. If, however, the asymptotic concentration is well above the remedial goal, it is an indication that the mass transfer has become diffusion-limited. This often occurs because mass transfer from within matrix blocks towards airflow pathways is controlled by very slow rates of aqueous-phase diffusion (McWhorter 1995; Baker et al. 1999). These effects have major ramifications for technology screening, pilot testing, design, operation, and shutdown, and will be addressed in later chapters.

(2) Dissolution. The degree to which a compound can dissolve into the aqueous phase is determined by its solubility. Since MPE involves removal of the liquid phase, contaminant mass will be removed with extracted water, but typically to a much lesser degree, over the first months or even year of an MPE remediation, than that which is extracted as vapor. Related factors strongly influencing dissolution of NAPL are the surface area of NAPL that is in contact with water, and the rate of aqueous flow through the NAPL zone. For contaminants trapped in saturated portions of the smear zone, dissolution rather than volatilization becomes the primary mass transfer mechanism, unless the water table is drawn down to expose the contaminants to air flow, or unless a related technology such as in situ air sparging (IAS) is employed in a way that ensures good contact between sparged air and aqueous or non-aqueous phase contaminants.

(3) Adsorption. Compounds in solution have a tendency to adsorb to the surfaces of soil particles or organic matter. The extent to which they do so depends on their partitioning coefficients and the specific surface and organic content of the soil or aquifer materials concerned. Organic compounds of higher molecular weight, for example, tend to have larger octanol-water partitioning coefficients, than those of lower molecular weight. In addition, the higher a soil's clay or organic matter content, the greater is its capacity to adsorb contaminants. While adsorption reactions tend towards equilibria and may be reversible, it typically takes longer for a given mass of contaminant to desorb than it took for it to adsorb, and some of the adsorbed contaminant mass can become effectively sequestered in recesses of the soil. Contaminants at such sites of sequestration may thus not be as susceptible to volatilization, dissolution or leaching, nor as bioavailable as might be indicated by an analysis of the total compound present using an aggressive extractant. Changes in subsurface geochemistry, however, can cause shifts in the equilibria, with the result that a compound thought to be unavailable can become more so at some future time.

(4) Biodegradation. Many organic contaminants are susceptible to being degraded biologically. They may be directly consumed by microorganisms that can make use of such compounds metabolically, or they may be degraded gratuitously by enzyme systems that serve some other normal metabolic purpose. The latter process, termed cometabolism, is generally not as prominent as the former. Biodegradation of many petroleum hydrocarbons occurs at much faster rates under aerobic conditions than when oxygen is limited. Thus, any process such as MPE that tends to increase airflow through the subsurface can somewhat enhance aerobic degradation of biodegradable compounds, including both amenable

VOCs and SVOCs. This is one of the primary processes underlying bioslurping. By contrast, many halogenated ethenes, while not susceptible to aerobic biodegradation except under a relatively narrow set of conditions, can undergo reductive dehalogenation under suitable anaerobic conditions. In many cases, natural attenuation, particularly processes that occur biologically, will be relied upon to accomplish whatever remediation remains upon cessation of MPE activities. It is beyond the scope of this document to review the extensive background literature on the topic of biodegradation, but salient considerations will be discussed within most of the chapters that follow.